



# CHEMICAL ABSTRACTS

Vol. 16.

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## 1—APPARATUS

C. G. DERRICK

**Thermometric anemometer.** J. S. G. THOMAS. *Phil. Mag.* 43, 688-98(1922); cf. *C. A.* 16, 1530. S. C. L.

**A new calorimetric bomb.** W. A. ROTH. *Brennstoff Chem.* 3, 104-5(1922).—The bomb is made of Krupp V<sub>3</sub>A-steel (20-23% Cr, 8-9% Ni, 0.1-0.3% C, austenitic), inlet and outlet tubes being pure Ag covered with a protective coating of molten AgBr. The metal dissolved during a detn. averaged 0.23 mg. Fe, less than 0.02 mg. Ag, no Ni detectable. W. B. V.

**An improvised electric thermostat constant to 0.02°.** S. C. BRADFORD. *Biochem. J.* 16, 49-52(1922).—The new feature is the kind of stirrer employed. It cannot be described briefly. BENJAMIN HARROW

**An apparatus for the rapid measurement of surface tension.** R. G. GREEN. *J. Bad.* 7, 367-70(1922).—An app. called the surface tension balance is described for the rapid measurement of surface tension by the drop-weight method. It consists of a dropping pipet, a delicate torsion balance, and an adjustable scale upon which the surface tension is read directly in dynes per cm. JOHN T. MYERS

**New stalagmometer or guttometer.** F. ESCHBAUM. *Ber. pharm. Ges.* 31, 211-9 (1921).—In estimating the surface tension of liquids by the drop method, the rate of outflow must not exceed 14 to 16 drops per min., a condition usually attained by providing the instrument with a sufficient length of capillary tubing. The same result is more readily secured by the following device. The upper end of the stalagmometer or guttometer consists of a glass stopcock having an opening on one side, the barrel of which has grooves running parallel to its length and communicating with each other at both top and bottom. A portion of the surface remains smooth so that the stopcock may be completely closed. On turning the barrel, the air in passing to the top of the liquid can be directed through any desired length of capillary, thus regulating the outflow of liquid accurately. The paper includes tables for calcg. guttometer estns. to stalagmometer measurements, and for normalizing any guttometer readings. In corrections for temp., every increase of 1° in the atm. temp. the drop wt. (guttometer) decreases by 0.25%, while the drop number (stalagmometer) increases by 0.25%. W. O. E.

**Modern preparation of aqueous ammonia.** GG. ILLERT. *Chem. App.* 9, 77-8 (1922).—A description, with 1 cut, of the Hirzel app., which will make practically c. p. solns. up to 30% NH<sub>3</sub> from crude liquors of 1-2% NH<sub>3</sub>. J. H. MOORE

**New form of high-vacuum automatic mercury pump.** H. P. WARAN. *Proc. Phys. Soc. (London)* 34, 120-5(1922).—In this modified Sprengel pump the Hg is lifted from the lower to the upper reservoir by a current of dry air sucked through a side tube by a filter pump. An intermediate reservoir in the middle of the fall tube, kept automatically exhausted by the Sprengel action in the lower fall, allows the upper half to exert a positive exhaustion for every pellet of Hg falling down, even at the lowest attainable pressure. This arrangement allows a tube of fairly large bore to be used for

the fall tube, and gives speeds and efficiencies of exhaustion comparable to those of the Gaede pump though requiring less than 0.5 g. of Hg. C. C. VAN VOORHIS

**Defect in the Sprengel pump.** J. J. MANLEY. *Proc. Phys. Soc. (London)* **34**, 86-91(1922).—The usual defect, the gas skin on the interior surfaces, is practically overcome by means of  $\text{CO}_2$  and KOH. Two adjuncts, one to provide for the use of a manual pump for the preliminary exhaust, and the other to facilitate the introduction of gases, are illustrated and described in connection with an elaborated form of the pump.

C. C. VAN VOORHIS

**Glass-lined tanks.** G. F. KROHA. *Ungerer's Bull.* **3**, 21-2(1922).—The gradual development of the industry, the construction of the various forms and the final coating with glass are described in considerable detail. W. O. E.

Cooling liquids (Brit. pat. 176,469) 13. Alloy for chemical apparatus (U. S. pat. 1,415,233) 9.

**Rotary filter.** J. S. BATES. U. S. 1,415,850, May 16.

**Filter press with a rotary filter.** R. D. LUCAS. U. S. 1,415,461, May 9.

**Apparatus for moisture determinations.** F. E. GREENWOOD. U. S. 1,415,546, May 9. The app. is adapted for moisture detns. in wood or similar materials; it comprises a flask, in which the material is heated, connected with a condenser discharging into a graduated measuring tube.

**Apparatus for separating gases from liquids.** H. FOTHERGILL. U. S. 1,416,632, May 16. The app. is adapted for removing air from boiler feed  $\text{H}_2\text{O}$ .

**Separating substances by fractional condensation.** SELDEN CO., J. M. SELDEN and C. G. SELDEN. Brit. 173,789, July 5, 1920. App. for the fractional condensation of mixed vapors, for instance, anthraquinone and anthracene, or phthalic anhydride and naphthalene, comprises a series of chambers, arranged one within another, having capacities increasing successively from the center outwards, and provided with means for separately withdrawing the condensed materials, the vapors being led first into the innermost chamber, in some cases from a vaporizer located therein. A suitable construction is specified.

**Separating substances by fractional sublimation.** SELDEN CO., J. M. SELDEN and C. G. SELDEN. Brit. 174,013, July 5, 1920. App. for the fractional condensation of mixed vapors, for instance, anthraquinone and anthracene, or phthalic anhydride and naphthalene, comprises chambers which are spaced apart, are connected in series, and contain perforated screens. Each chamber may also contain a cooled baffle, consisting, for instance, of a flat open vertical tube, situated a little nearer the inlet than the outlet, and extending to within a short distance of the side walls. A perforated screen may be placed on one side only or on each side of the baffle, and may be suspended from a bar. By means of handles and rods the screens may be swung against stops so as to shake off deposits. Doors are provided in the casings and connecting conduits. Cf. 173,723 (C. A. 16, 1341) and 173,724.

**Analyzing gases.** H. A. DAYNES and CAMBRIDGE & PAUL INSTRUMENT CO., LTD. Brit. 176,574, Jan. 8, 1921. The gas-analyzing app. described in 124,453 (C. A. 13, 1550), in which a pair of electrically heated wires forming part of a Wheatstone bridge are for comparison surrounded by the gas to be tested and a standard gas, is provided with means whereby both of the gases are satd. at the same temp. with an extraneous constituent such as  $\text{H}_2\text{O}$  vapor, to eliminate the errors arising from the presence of such constituent. In the case of flue gases, the app. is adapted to eliminate the effect of  $\text{H}_2\text{O}$  vapor by enclosing in the cavity contg. the standard gas, an excess of  $\text{H}_2\text{O}$ , and

by cooling the app. or the gases so that when under test the latter are satd. with  $H_2O$  vapor.

**Drying machine.** CHÔJIRÔ NISHIO. Jap. 39,168, July 7, 1921. Diagrammatical description. Wooden frames having many horizontal shelves are moved gradually from the front to the rear. Air is supplied by elec. fans fitted to both side walls of the room.

**Drying apparatus.** NAOJI IMAFUJI. Jap. 39,286, July 16, 1921. Diagrammatical description. Hot air is supplied to the falling substance from the side walls.

**Centrifugal oil purifier.** M. LEITCH. U. S. 1,415,881, May 16.

## 2—GENERAL AND PHYSICAL CHEMISTRY

W. E. HENDERSON AND EDWARD MACK

**Prof. Dr. Karl Hopfgartner (1868-1921).** J. ZEHENTER. *Oesterr. Chem. Ztg.* 25, 67-8(1922).—An obituary.

E. J. C.

**Falsifications in the history of early chemistry.** J. M. STILLMAN. *Sci. Monthly* 14, 560-7(1922).—Notable instances are given of alchemical works falsely attributed to prominent philosophers and scientists of an earlier time.

A. M. P.

**The chemically trained man and citizenship.** R. E. CHASE, JR. *Chem. Age* (N. Y.) 30, 210(1922).

E. J. C.

**The role of the physicist in the development of chemical theory.** JAMES WALKER. *J. Chem. Soc.* 121, 735-45(1922).—An address.

E. J. C.

**Atomic weight of isohelium.** MAXIMILIAN C. NEUBURGER. *Physik. Z.* 23, 145-6(1922).—From the max. possible deviations of the at. wts. of O, N and C from 16, 14 and 12 and considerations of the probable constitution of their atoms it is argued that the most probable value of the at. wt. of isohelium (Rutherford's  $X_2$ ) is 3.0011 corresponding to an atomic mass of  $4.95 \times 10^{-12}$  g.

E. D. WILLIAMSON

**The conjugation of partial valencies.** ROBERT ROBINSON. *Mem. Proc. Manchester Lit. Phil. Soc.* 64 [4] 1-14(1920).—The hypothesis previously described (*C. A.* 11, 249, 250; 12, 141, 2313; 13, 3150) is applied to various types of chem. reactions of C compds.

J. C. S.

**Determining properties of matter.** M. D. HERSEY. *J. Wash. Acad. Sci.* 12, 167-72(1922).—This purely theoretical discussion stresses the point that in detg. a relative property it is not necessary to use expts. in which the observed action is directly proportional to the property in question or even uniquely detd. by it. The appropriate dimensionless equation must be developed and by means of a few expts. the value of the observed quantity interpolated for the same values of the dimensionless variables as obtained for the standard sample.

E. D. WILLIAMSON

**Ozone.** E. H. RIESENFIELD AND G. M. SCHWAB. *Naturwissenschaften* 10, 470-1 (1922).—Liquid ozone (A) is non-explosive when free from impurities like  $Et_2O$  which act catalytically to effect decompn. This agrees with the results of Erdmann but not with those of Dewar and Ladenburg. A mixt. of liquid O (B) and A cooled below  $-158^\circ$  sepd. into 2 layers: (1) a light blue soln. of A in B, and (2) a deep blue soln. of B in A. Above  $-158^\circ$  the liquid was homogeneous. Dists. *in vacuo* below  $-158^\circ$  a residue of A contg. 30% B was obtained. Fractional distn. of the latter soln. yielded a liquid contg. 0.5 mol. A per 1 mol. B. The vapor d. of the gas from this liquid corresponded to  $O_3$ . By cooling this gas with liquid H, bluish black crystals were obtained, m. slightly abv  $-250^\circ$ . Evapn. of the melted crystals gave an intensely deep blue gas. The crit. temp. was  $-13^\circ$ . Since it was uncertain whether slight decompn. occurred, the crit. temp. of pure A was estd. to be a few degrees higher. The phys. consts. of pure liquid  $O_3$  were thus found to be approx.: m. p.  $-250^\circ$ , b. p.  $-110^\circ$  and



crit. temp.  $-10^{\circ}$ . The great difference in the phys. consts. of A and B excluded the possibility of the presence of a third modification, e. g.,  $O_3$  with properties similar to those of A.

C. C. DAVIS

Density and temperature. III. W. HIGAZ. *Z. Elektrochem.* 28, 116-8(1923); cf. *C. A.* 13, 2791.—The d. of the satd. vapor of homologous compds. at the b. p. increases with the mol. wt. The d. differences also increase in the same order. In the case of higher homologs the ratio of the d. of the satd. vapor to that of the liquid at first decreases with rising temp. and then increases. In homologous series the d. ratio of a liquid and its satd. vapor at a definite temp. increases with the mol. wt. of the homolog.

H. JERMAIN CRIGHTON

A microscopic arrangement for the examination of opaque crystals. M. FRANÇOIS AND CH. LORMAND. *Bull. soc. chim.* 29, 366-74(1921).—No contrivance has previously been devised for rendering visible microscopically very small opaque or deeply colored crystals in all their details without deformation, halo or false colors. Various methods led to the development of 2. Lateral illumination by an incandescent Pt wire permitted perfect vision with objectives 7 and 8 but was discarded because of frequent fusion of Pt and heating of both the crystals and the objective. The method adopted consists of (1) an ordinary microscope with its objectives fitted on their lower face with a Ag concave mirror pierced by a hole; (2) an incandescent light placed in the microscopic axis with its rays rendered parallel to the axis by a lens; and (3) a glass slide with an opaque disk on which rest the crystals protected from the light passing from beneath. The curvature of the mirror must be such that the reflected light converges on the object, and consequently each objective must have its own mirror. The width of the mirror should be equal to or less than its radius of curvature. The opaque disks are made of various colors depending on the crystals, and vary from 0.75 to 3.0 mm. in order to cover the field of any size of objective. The source of illumination can be a 2-3 v. lamp 1-2 cm. diam. set in an eye-piece so that the lens renders the rays parallel. Directions are given for the mech. construction of the complete contrivance. Crystals of Fe, Cr and Ni silicides,  $Hg_2NI$ ,  $Hg_7H_2NI_4$ ,  $HgS$ , etc., have been photographed by this method with remarkable results.

C. C. DAVIS

Photosensitiveness of arsenic trisulfide sols. H. FREUNDLICH AND A. NATHAN-SOHN. *Kolloid Z.* 28, 258-62(1920).—Sols of  $As_2S_3$  are photochemically active. They sensitize the oxidation of color substances, such as eosin and malachite green, in light. The formation of colloidal S by illuminating  $As_2S_3$  sols depends on this photochem. sensitization, for the  $H_2S$  which is set free by the hydrolysis of the  $As_2S_3$  is oxidized to S through the sensitizing action of the trisulfide micellae. Mixtures of As sulfide sols and S sols are, according to Odén, unstable, although both are negatively charged. Both sols are amicroscopic, but on mixing under an ultramicroscope it is seen that the micellae speedily become much larger. Consequently, the mixt. of the sols is more sensitive to electrolytes than the individual sols; the coagulation values of  $HCl$  and  $Al(NO_3)_3$  are less than half that for pure As sulfide sol and still smaller than that for pure S sols. This instability depends probably on a mutual action of the sols on one another since the As sulfide sol contains in all probability  $H_2S$  or a polysulfide as active electrolyte, while the colloidal S contains pentathionic acid. Pentathionic acid and  $H_2S$  in the presence of one another are unstable and react with the formation of S. The reaction robs the micellae of both sols of their active electrolytes and reduces the stability. The As sulfide sol is more sensitive to electrolytes after illumination because colloidal S is formed in it, and colloidal S which contains As sulfide sol after illumination exhibits a smaller coagulation value toward electrolytes, even in the dark. J. C. S.

Method for the determination of the surface of adsorbing powders. F. PANFILI. *Z. Elektrochem.* 28, 113-5(1922).—The method is based upon the adsorption of a radio-

active element (cf. C. A. 9, 1875). In expts. carried out with finely divided  $\text{PbSO}_4$  as adsorbent, an isotope of Pb (ThB) was employed as the "radioactive indicator." During adsorption the isotope replaces Pb atoms on the surface of the adsorbent, these atoms entering the soln. (cf. C. A. 9, 553). The distribution of the isotope between the adsorbent and the soln. is detd. by means of an electroscope, and the surface of the adsorbent calcd. from the adsorption equil. Since the ratio of the quantity of isotope adsorbed to that in soln. is equal to the ratio of the surface of the element (Pb) to the quantity of this element in soln., and since the first ratio can be detd. by the electroscopic measurements and the quantity of the element in soln. can be detd. analytically, the surface of the element is readily calcd. This surface is expressed in mols. From exptl. data values for the sp. surface of  $\text{PbSO}_4$  are obtained which are approx. double the values detd. by microscopic measurements.

H. JERMAIN CRUGHTON

Adsorption and solubility. G. GEORGIEVICS. *Kolloid Z.* 28, 253-4 (1921).—A criticism of a paper, under the same title, by Lundelius (C. A. 14, 2117) in which G. directs attention to some previous work on the relationship between adsorption and the other properties of the solvent and the dissolved substance (C. A. 6, 2349; 7, 2880). Several other points on which the work of G. is at variance with that of Lundelius are mentioned and criticized.

J. C. S.

A formula for the viscosity of liquids. H. B. PHILLIPS. *Proc. Nat. Acad. Sci.* 7, 172-7 (1921); *Science Abstracts* 25A, 111-12.—P. obtains for the viscosity of a liquid the formula  $\eta = (nNh)/2M(v-\delta)$ , where  $N$  is the number of mols. in a mol,  $h$  is Planck's const.,  $M$  is the mol. wt. of the liquid in the gas phase,  $v$  its vol. per g., and  $n$  an integer. The quantity  $\delta$  is the co-vol. as used in the equation of state of Keyes,  $p = [RT/(v-\delta)] - [A/(v-\delta)^2]$ . In all cases to which the formula has been applied,  $n = 6$ , and so the above expression takes the form  $\eta(v-\delta) = 3Nh/M$ . It is to be noted that  $3N/M$  is the number of translational degrees of freedom of the mols. in the vol.  $v$  of the liquid. The expression is proved in section 2 of the paper. Owing to lack of data on the equation of state, the only substances on which the formula can at present be tested are  $\text{CO}_2$ , ether and Hg. At low temps. the measured and calcd. viscosities do not differ by more than the exptl. error. In the case of  $\text{CO}_2$ , the temp.  $30^\circ$  is too near the crit. point ( $t = 31^\circ$ ) for satisfactory use of the equation of state. Above  $10^\circ$  the calcd. viscosity of ether is too large, the difference increasing with the temp. This may be due to the fact that ether is a complex of more than one type of mol. The equation of state was detd. on the assumption that each liquid mol. is formed by the combination of two gas mols. This may be substantially true at  $10^\circ$  and not at  $100^\circ$ . To obtain values of  $v-\delta$  for Hg, use is made of the fact that monatomic substances seem to have const. co-vols.  $\delta$ ; therefore for Hg, which is monatomic in the gas phase,  $\delta$  is assumed to be const. or nearly const. in the liquid phase. Since the term  $RT/(v-\delta)$  is very large for Hg,  $p$  may be neglected at atm. pressures, and therefore  $\sqrt{[(v-\delta)T]} = 3(v-\delta)$ , where  $c$  is const. Below  $100^\circ$  the difference of the calcd. viscosities and those measured is not greater than the difference between the values obtained by different observers. At higher temps. the calcd. viscosities are consistently smaller than those measured. The observations, however, differ greatly, owing probably to oxidation of the Hg in contact with the air. The result may be to increase the viscosity to almost any amt. Tables of data are included (cf. Keyes, C. A. 11, 2846).

H. G.

Theory of formation of liquid crystals or crystalline liquids and their properties—elements of crystals and nucleus of crystals. E. YAMAZAKI. *J. Chem. Soc. (Japan)* 43, 134-54 (1922).—A theoretical paper. Previous work is reviewed. The liquid cryst. state is not a third phase, independent of solid and liquid phases, but is a transitional phase appearing during progressive changes from liquid to cryst. and vice versa. When a liquid is subjected to a temp. below the m. p., and its energy content thus diminished,

mol. vibration is lessened, while mol. attractive force becomes more effective. In such a state, there will be formed, in certain parts of the liquid, certain mol. aggregations which maintain their own special arrangement which Y. calls the "element" of crystals. Since the speed of crystn. is greater at a higher temp., somewhere around the m. p. there is an optimum temp. when the speed of crystn. is a max. Relation between the temp. at which the element is formed and the temp. at which the max. rate of crystn. exists, is an important factor in detg. the formation of liquid cryst. When the "element" of crystals has a very small rate of crystn., a transparent cryst. liquid (Vorländer) is formed, and when its speed is greater, a turbid cryst. liquid. When the speed is exceedingly great, some crystallizes directly, the other crystallizes after passing through an oily state, a phenomenon controlled not only by the speed of crystn., but also by the magnitude of the mol. attraction working among the mols. and perhaps by other factors. Phys. appearance of liquid cryst. as an apparent independent phase should be explained by Nernst's interpretation. The case where an ordinary substance does not form any cryst. liquid unless foreign crystals are added, is due to lowering the max. temp. of speed of crystn., and raising the temp. of formation of the "element" of crystals and nucleus of crystals.

S. T.

Studies of the constitution of soap solutions. Solutions of sodium palmitate, and the effect of excess of palmitic acid or sodium hydroxide. J. W. McBAIN, MILICENT TAYLOR AND MARY E. LAING. *J. Chem. Soc.* 121, 621-33(1922).—The cond. (cf. *C. A.* 5, 2360) of NaOH solns. diminished almost linearly with addn. of increasing amts. of palmitic acid to the compn. sodium palmitate (NaPal), at which point there was a break in the curve and then the cond. again fell linearly to the compn. 2NaPal.HPal. Further decrease of cond. was unimportant. Osmotic data obtained by the dewpoint lowering method (cf. *C. A.* 14, 1918) gave results very similar to those of cond. The concn. of crystalloid steadily decreased as the NaOH was changed to NaPal by addn. of HPal and almost disappeared at the compn. 2NaPal.HPal. Colloidal acid soaps and not free HPal were evidently the products of hydrolysis of NaPal at 90°. The most neutral of the series of acid soaps which ranged down to NaPal, HPal and beyond corresponded to the empirical formula 2 NaPal.HPal. A method is given for calcg. from cond. and osmotic activity the concn. of each of the constituents present in soap solns. at various concns. The addn. of an electrolyte such as NaOH rapidly increased the amt. of neutral colloid and almost eliminated crystalloidal soap, though an appreciable proportion of ionic micellae remained.

H. M. McLAUGHLIN

The effect of electrolytes on the constitution of soap solutions, as deduced from electromotive force. C. S. SALMON. *J. Chem. Soc.* 121, 711-5(1922).—The concn. of both ions of the electrolytes, KCl and NaCl, added in amts. insufficient for salting out, was measured by means of the e. m. f. The excess of alkali over the Cl<sup>-</sup> gave the proportion of soap present as ionic micellae. Since the presence of a common ion prevented the dissociation of the colloidal electrolyte, soap solns. contg. KCl or NaCl were found to be largely in the form of undissociated neutral colloid. The activity of the Cl<sup>-</sup> in KCl solns. appeared to be unaffected by the addn. of large amts. of K laurate owing to the compensating effect of the increase of bulk and of the removal of solvent through hydration of the soap.

H. M. McLAUGHLIN

The minimum solubility of aluminium hydroxide in water. A. MASSINK. *Chem. Weekblad* 19, 66(1922).—To explain the differences in the results of Am. investigators (A. Wolman and F. Hannan and also Blum) and those of Ada Prins and of Van de Sande Bakhuizen, it is pointed out that the former did not use chemically pure H<sub>2</sub>O while the latter took this matter into consideration.

VINCENT VERMOOTEN

New conceptions of electrolytes. I. The degree of dissociation of acetic acid in water and in salt solutions. ERLING SCHREINER. *Z. anorg. allgem. Chem.* 115,

181-203(1921).—A theoretical paper in which formulas are derived for correcting the dissoc. const., as ordinarily detd. from cond. measurements, for the viscosity of the soln., inter-ionic force, and the activity of the water, that is, the hydration of the H ion. The cond. of AcOH as detd. by different observers is thus corrected at 25° over the range of diln. from 0.0005 to 2.6 normal. The law of mass action is shown to hold up to the highest concn. From potential measurements at 18° and 25° of AcOH solns. contg. NaOAc or other salts, the activity of the acetate ion and the dissoc. const. of AcOH have been calcd. Such measurements do not, as has been generally supposed, det. the H-ion concn., but the activity of the H ions, which is associated only with the non-hydrated ions. The dissoc. const. of AcOH calcd. thus agree well with those calcd. from the cond. measurements. Taking the activity const. of the H ion as 0.2, that of the acetate ion is the same in NaOAc soln. and 0.3 in Na and K chloride solns. II. The introduction of a catalysis coefficient in hydrogen-ion catalysis. *Ibid* 116, 102-116.—In catalytic reactions such as the hydrolysis of esters or the inversion of sucrose by acids, assuming complete dissoc. and that only the H ions are active, the reactive velocity should be proportional to the concn. Actually, however, the catalytic effect at higher concns. is greater, and a similar accelerating effect is produced by the addition of neutral salts. It is shown that, by the introduction of a catalysis coeff.,  $f_h$ , this extra catalytic effect can be accounted for. The new coeff. is found to be the reciprocal of the cond.-viscosity coeff.,  $f_\mu$ , which is the ordinary cond. coeff. corrected for the viscosity of the electrolyte. The ratio  $v/C$ , where  $v$  is the reaction velocity and  $C$  the acid concn., thus corrected to  $v f_h / C$ , gives a very good const. in the hydrolysis of acetates by HCl alone and in presence of neutral salts, in the inversion of sucrose, and in the keto  $\rightarrow$  enol acetone transformation. The degree of dissoc. of weaker acids, such as dichloroacetic or cyanoacetic acid, can be calcd. from catalysis measurements, and the results agree very closely with those calcd. from cond. measurements. J. C. S.

Application of Dalton's law to concentrated solutions. RADU CERNATESCU. *Ann. sci. Univ. Jassy* 10, 259-92(1920).—The f.-p. depressions of pairs of nonelectrolytes were detd. separately and when mixed for the same solvent. The osmotic pressure of the mixt. may be less or greater than the sum of the osmotic partial pressures. The relation of the osmotic pressure to the sum of the partial pressures may also be reversed with increase or decrease of concn. The Abegg formula is inadequate, and the facts can only be explained with the help of van der Waals' theory. A new formula for the osmotic pressure of mixts., based on the modified Nernst formula of Bogdan (*Ann. sci. Univ. Jassy* 10, 25-84) is devised. The anomalies observed in f.-p. depressions with strong electrolytes are probably due also to the fact that observed depressions are not equal to the sep. partial depressions. J. C. S.

The partial miscibility of liquid couples. Applications to the study of reactions in solution. RENE DUBRISAY. *Ann. chim.* 17, 222-56(1922); cf. *C. A.* 16, 1526.—A method of physico-chem. analysis based on the reciprocal soly. of liquids is described. The neutralization of HCl,  $H_2SO_4$ ,  $H_3PO_4$ ,  $H_2CO_3$ , AcOH, succinic acid and tartaric acid with NaOH is described and the existence of  $NaHSO_4$ ,  $Na_2SO_4$ ,  $NaH_2PO_4$ ,  $Na_2HPO_4$ , and  $Na_2PO_4$  in soln. is proved. The action of HCl on  $Na_2SO_4$ , the formation of double sulfates in soln. and the action of  $H_3BO_3$  on polyalcohols has also been studied by the aid of the reciprocal soly. of  $H_2O$  and PhOH. T. E. DUNLAP

Electrolytic dissociation of dicyanodiamide in aqueous solution. NAOTO KAMEYAMA. *J. Chem. Ind. (Japan)* 24, 1263-7(1921).—By measuring elec. cond. of solns. composed of NaOH and  $C_2N_2H_4$  in various proportions, the following conclusions are reached.  $NaC_2N_2H_4$  is hydrolyzed 94.5% in 0.1 M soln., and practically completely in less concd. soln. Its hydrolytic const. is 2.0 and dissoc. const. is  $0.6 \times 10^{-14}$  at 25°. Its basicity is also extremely small, as its hydrochloride, if formed, is completely hydrolyzed in aq. soln. S. T.

Ethyl carbonate as an amphoteric electrolyte. H. V. EULER AND O. SVANBERG. *Z. physiol. Chem.* 115, 139-46(1921).—The acid and basic dissociation consts. are about  $10^{-15}$  and  $10^{-20}$ , resp.

R. L. STEELE

Plea for rational interpretation of hydrogen-ion measurements. WM. C. MOORE. *Trans. Am. Electrochem. Soc.* 41 (preprint April, 1922).—In many biological systems H-ion regions are of more importance than actual H-ion concns. Thus invertase has a flat max. of activity in the range for  $[H^+]$   $1 \times 10^{-4}$  to  $1 \times 10^{-6}$ , and, concurrently, fermenting molasses mashes show within this range no relation between H-ion concn. and yield of ethanol. Finally, a plea is made to express H-ion concns. in any one set of measurements in terms of a common denominator instead of as " $p_H$ ," values which for chem. work sometimes are inconvenient.

C. C. VAN VOORHES

Chemical kinetics of the system: reductase-methylene blue. E. YAMAZAKI AND H. KANEKO. *J. Chem. Soc. (Japan)* 42, 90(1922).—Velocity of the reaction between reductase (Schardinger) and methylene blue in presence of aldehydes was studied by the method of Bredig and Sommer (*C. A.* 4, 1408). 0.2-0.3% aq. solns. of Merck's methylene blue, fresh milk shaken with toluene as reductase (Schardinger), 2% of gelatin as a protective colloid and  $CO_2$ - $NaHCO_3$  as buffer were used. The dye was estd. by adding an excess of  $SnCl_2$  and titrating the remainder with  $FeCl_3$ . The reaction and titration were conducted in an atmosphere of  $CO_2$  or N. The results follow: (1) Velocity const. with variable concn. of the enzyme with salicylaldehyde (A) and *p*-tolualdehyde (B). To 30 cc. dye (0.3%), 5 cc. 0.01 N  $NaHCO_3$ , 5 cc. gelatin various amts. of milk (F) are added and made up to 128 cc. The velocity consts.  $kE$  for F = 64, 32, 16, 8, 4 with B are, resp., 0.00849, 0.00319, 0.000403, 0.000214, 0.000106 and  $kE/F$  are 0.000133, 0.000099, 0.000025, 0.000027 and 0.000027. The results are similar to those obtained with colloidal Au soln. (B. and S.). Under exactly identical conditions. B gave  $KE/F = \text{const.}$  (0.000103). (2) Concn. of dye (S) is variable. For this only B was tried. The velocity consts. obtained from these expts. when plotted against  $t$  show that when S is great  $kE$  is small, showing that the dye inhibits the enzymic action. Unless S is very small the enzyme suffers instantaneous irreversible inhibition, analogous to diastase. Thus  $[E] + [S] = [Z]$  should hold here (cf. *C. A.* 16, 1965) and therefore  $KE'/K+S$  should be const. The calcd. value  $[(K+S)/KE']_{t=0}$  from the data are for S = 50, 40, 30, 20, 10, 5, resp.: 0.180, 0.201, 0.216, 0.201, 0.170, and 0.218. (3) When aldehyde concn. is variable. The max. const. was obtained when the soln. (128 cc.) contains 1 cc. of the aldehyde (B was used). The temp. coeff. is calcd. to be 4.97. Effect of  $H^+$  and  $OH^-$  also are studied and discussed.

S. T.

Chemical reactions caused by the silent discharge. I. Ethylene and nitrogen. II. Benzene and carbon dioxide. S. MIYAMOTO. *J. Chem. Soc. (Japan)* 43, 21-48 (1922).—The app. is so constructed that the desired gases can be introduced at the bottom, and the gaseous products can be let out from the top of the chamber. The solid and liquid products are held in the app. (I)  $C_2H_4$  and N. N was prepd. from  $NH_4Cl$  and  $NaNO_2$ ;  $C_2H_4$  from alc. and concd.  $H_2SO_4$ . These gases were mixed in the ratio of 2:1 and passed through alk.  $CaCl_2$  before being subjected to the discharge. When 15 l. of such mixt. were passed through 4 similar app. (once), during 6 hrs., 3.53 g. of liquid products were formed; they consisted of a nitrile,  $C_{15}H_{11}CN$ , an amine,  $C_{20}H_{13}N_4O_2$ , which is probably an oxidized product of the amine  $C_{20}H_{13}N_4$ , and unsatd. hydrocarbons,  $C_{10}H_{10}$ ,  $C_{12}H_{12}$ ,  $C_{14}H_{14}$ ,  $C_{16}H_{16}$ ,  $C_{18}H_{18}$ . Among the gaseous products, HCN and  $CH:CH$  were identified. When the reaction was continued for several months, the inside of the chamber became coated with a solid compd.  $(C_{20}H_{13}O)_n$ , which is probably formed by oxidization of a polymer of the unsatd. hydrocarbons (II)  $C_6H_6$  and  $CO_2$ . From this mixt. a phenol,  $C_{10}H_8O$ , was isolated. The probable explanation for these reactions is given.

S. T.

**Influence of intensive drying on internal change.** A. SMITS. *Z. physik. Chem.* 100, 477-8(1922).—A brief discussion of Bakers' observations regarding the influence of drying on the b. ps. of  $N_2O_3$  and  $N_2O_4$  (cf. *C. A.* 7, 1332). H. JERMAIN CREIGHTON

**Velocity of decomposition of silver permanganate.** A. SIEVERTS AND H. THEBRATH. *Z. physik. Chem.* 100, 463-76(1922).—The decompn. of  $AgMnO_4$  takes place chiefly in accordance with the equation  $AgMnO_4 = AgMnO_3 + O$ . In the presence of  $H_2O$  the residual  $AgMnO_3$  combines with  $1/2$  mol.  $H_2O$ . The course of the reaction at  $30^\circ$  can be expressed approx. by the equation for an autocatalytic reaction:  $dx/dt = Kx(a-x)$ . The decompn. product, regarding the chem. nature of which nothing has been detd., accelerates the reaction in proportion to its mass. The value of the velocity const. varies with the mode of prepn. of the  $AgMnO_4$ . The presence of  $H_2O$  exerts a marked influence on the reaction. Dry  $AgMnO_4$  decomposes very slowly even at  $50^\circ$ . Traces of  $H_2O$  bring about a large increase in the velocity of decompn., while more  $H_2O$  has but little influence. Addns. of pumice and the decompn. product change only the initial velocities. The influence of temp. is important. At  $0^\circ$  the reaction ceases completely, even in the presence of  $H_2O$  and the products of decompn. At  $50^\circ$  the reaction cannot be represented by the same equation as at  $30^\circ$ . The  $x, t$ -curves for  $50^\circ$  are characterized by a long, almost linear portion. H. J. C.

**Dissociation of chlorine.** H. V. WARTENBURG AND F. A. HENGLEIN. *Ber.* 55B, 1003-6(1922).—Measurements have been made of the pressure of pure Cl at a no. of temps. between 833 and  $1003^\circ$  abs. The Cl was prepd. by decomp.  $AuCl_3$ . The pressures varied between  $3.25$  and  $6.05 \times 10^{-3}$  mm., corresponding to a change in the degree of dissoc. from 10.3 to 72.4%. The exptl. values for the degree of dissoc. are in fair agreement with those obtained by calcul. The value 70,000 cal. at  $T = 0$  has been obtained for the heat of dissoc. of  $Cl_2$ . H. JERMAIN CREIGHTON

**Determination of high temperature by effusion of gases.** Y. YAMAGUCHI. *J. Chem. Soc. (Japan)* 43, 1-21(1922).—When iron dust is packed in a porcelain tube and reduced by H, the passage of the gas becomes more difficult as the temp. rises; in order to maintain a const. rate of flow of the gas, the pressure must be increased with the rise of temp. Y. constructed an app. to measure this excess pressure, and used it as a convenient method of measuring high temps. S. T.

**Molecular thermodynamics.** BERNARD CAVANAGH. *Phil. Mag.* 43, 606-36(1922).—An extended mathematical paper. In section I it is shown that a general treatment of the thermodynamics of any system of phases can be developed from the mol. theory with the use of certain broad assumptions. In II the meaning and value of the mol. treatment are discussed, and it is shown how this treatment paves the way for the introduction of dynamic theory as an aid to the soln. of the general problem. In III a slightly modified procedure, useful in many practical cases, is introduced and the significance of the chief types is demonstrated. IV contains a special treatment of polymerized and mixed solvents. In V the question of electrolytes is considered from the point of view of thermodynamics. The question of weak and "semi-strong" electrolytes is treated as an example of the participation of ions in chem. reactions. S. C. L.

**Polymerization at the critical temperature.** WM. R. FIELDING. *Chem. News* 124, 182-4, 197-9, 213-5(1922).—From data from Landoit-Bornstein's Tables F. detd. the degree of polymerization of many substances by means of the formula  $p = M P_c / k d_c T_c$ , in which  $p$  = the degree of polymerization,  $M$  = the formula wt.,  $d_c$  = the crit. d.,  $P_c$  = the crit. pressure,  $T_c$  = the crit. temp. and  $k$  is a const. whose value is found from the data for ether to be 10.5. F. E. BROWN

**Pressure-volume relation of superheated liquids.** K. L. WISMER. *J. Phys. Chem.* 26, 301-15(1922).—Pressure-vol. curves at const. temp. were exptly. obtained

for liq.  $(Et)_2O$  at 121.5°, 127.9°, and 133.8°, and for liq.  $EtCl$  at 99.6°, 109.7°, and 117.4° with a pressure range of about from 1 to 50 atm. Practically linear relations were obtained. Observations were also made of the min. pressures at which the ether remained liquid. The plot of these pressures against the temp. is a straight line passing through the critical point.

E. D. WILLIAMSON

**Latent heats of fusion. I. Benzophenone, phenol, and sulfur.** MRS. K. STRATTON AND J. R. PARTINGTON. *Phil. Mag.* 43, 436-46(1922).—A direct method was employed consisting in applying a known quantity of heat electrically at the m. p. until completion of fusion is indicated by a further rise of temp. The values obtained in g. cal. per g. are: for benzophenone 21.70, for phenol 29.06, and for monoclinic S 8.85. A theory of fusion from the quantum standpoint using Debye's formula for the energy, is presented and discussed. In some cases the existence of intramol. vibrations as well as rotation is shown to be probable in liquid mols.

S. C. L.

**An application of the electron tube to the measurement of weak alternating currents by means of the electrometer.** LUDWIG BERGMANN. *Z. Physik* 9, 369-71 (1922).

E. J. C.

**The conduction of electricity through fused sodium hydroxide.** A. FLICK AND T. WALLACE. *Trans. Faraday Soc.* 16, 346-59(1921).—The fused NaOH was contained in an iron vessel in the form of an inverted cone of nearly a ton capacity. The measurements were made by passing a varying d. c. between nichrome electrodes and measuring the corresponding voltage drop, then calcg. the resistance from Ohm's law. The electrodes were rectangular and varied in size from 2.54 cm. wide to 0.3 to 10.0 cm. long. They were held in an app. which permitted the distance between them to be varied. The following expts. were made: The effect of altering the distance between the electrodes; the effect of altering the size of the electrodes; the effect of change in temp.; and the decompn. voltage of fused NaOH. As the distance between the electrodes was increased the resistance increased to a max. value, after which it remained const. The resistance between 320°-480° decreased 0.102% per degree rise in temp. The decompn. potential varied from 1.952 v. at 480° to 2.332 at 320°.

W. G. FRANCE

**Electrical conductivity and density of aqueous solutions of electrolytes.** ADOLF HEYDWEILER. *Z. anorg. allgem. Chem.* 116, 42-4(1921).—The results of cond. and d. measurements of aq. solns. of about 60 metallic salts of inorg. and org. acids are given in tabular form. Cf. *C. A.* 15, 1252.

J. C. S.

**The resistance of electrolytes at high frequencies.** J. J. DOWLING AND KATHARINE M. PRESTON. *Phil. Mag.* 43, 537-45(1922).—Methods of utilizing high-frequency oscillation valve circuits for the measurement of high resistance have been devised, the principles being extensions of D.'s "ultra-micrometer" circuits. These methods are capable of great precision and are suitable both for metallic and electrolytic resistances. Preliminary tests indicate that ordinary electrolytes offer the same resistance to high- as to low-frequency currents. Observations on glycerol solns. which show anomalous "resistance-concn." variations for d. c. are somewhat inconclusive, but seem to show that this is more pronounced for high frequency.

S. C. L.

**Dielectric constants of some of the esters at low temperature.** L. C. JACKSON. *Phil. Mag.* 43, 481-9(1922).—A method is described for the detn. of the dielec. consts. of liquid or solid substances by the aid of triode valves. The results obtained for Me Et, *n*-Pr, and *n*-Bu formates and for the corresponding acetates at the temp. of liquid air are given and compared with the results of other investigators at ordinary temps. At low temps. the acid radical apparently contributes but little to the value of the dielec. const. Results showing the dependence of temp. for *n*-Bu acetate through the temp. range 292-80° Abs. are given and show that the const. increases linearly with decrease of temp. down to the m. p. where a sudden drop in the value occurs followed by a very gradual rise as the temp. is further lowered.

S. C. L.

A simple theory of the nephelometer. P. V. WELLS. *J. Am. Chem. Soc.* **44**, 267-76(1922).—Mathematical expressions for diffuse transmission and reflection are developed, and values obtained by them compared with exptl. results. It is shown that the depth ratios by reflection and transmission are equal. However, the two methods do not give the same results except in an intermediate range of concns.

G. W. STRATTON

The structure of chlorine dioxide and related compounds (PERKINS) 3. Lyotropic series and  $\beta$ -oxidation (SPIRO) 11A. The cleansing action of soap solutions (MUNS) 27. Discussion on the structure of molecules (LANGMUIR, *et al.*) 3. Electron theory of valence as applied to organic compounds (STIEGLITZ) 10.

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### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Twenty-five years of radioactivity. R. SCHMID. *Umschau* 25, 693-6(1921).—Address. D. C. B.

Radioactivity. ERNEST RUTHERFORD. *Engineering* 113, 299-300, 331-2, 365-6, 386-7, 414-5, 464-6(1921).—A report of six lectures delivered at the Royal Institution. L. D. R.

The new atomic weight tables and the science of the isotopes. EDMUND NEUSSER. *Oesterr. Chem. Ztg.* 25, 45-9(1922).—Historical review, of the present state of knowledge and the significance of isotopes. G. L. CLARK

Notes on the theory of radiation. C. G. DARWIN. *Phil. Mag.* 43, 641-8(1922).—Mathematical formulation of the relation between the optical and the thermodynamical descriptions of an arbitrary field of radiation. S. C. L.

Isotopy and the disintegration of matter. CRUT. *J. pharm. chim.* 25, 139-48(1922).—A review of the work of J. J. Thomson, F. W. Aston, and Brönsted and Hevesy (C. A. 16, 17). S. WALDBOTT

Rutherford's discovery of a new light atom nucleus. ADOLF SIEKAL. *Naturwissenschaften* 9, 77-82, 93-8(1921); cf. C. A. 14, 3570.—A discussion and criticism of Rutherford's discovery of the He isotope  $X_2$ . J. C. S.

A possible physical interpretation of Lewis and Adam's relationship between h, c, and e. G. A. NEWGASS. *Phil. Mag.* 43, 698-700(1922).—Cf. L. and A., *Phys. Rev.* [2] 3, 92(1914). S. C. L.

Polarization phenomena in X-ray bulbs. R. WHIDDINGTON. *Phil. Mag.* 43, 720(1922).—Criticism of Ratner (C. A. 16, 1043). S. C. L.

Atomic structure and the physical and chemical properties of the elements. NIELS BOHR. *Z. Physik* 9, 1-67(1922); cf. C. A. 16, 377.—A long address summarizing in non-mathematical form the results of the application of B.'s "correspondence-principle" to at. structure. There is also a review of recent work in the field. The formation of an atom of at. no. =  $N$ , is treated as  $N$  successive captures of single electrons by the nuclear field. In the ordinary arc and spark spectra of the elements one sees the last and next to last captures in progress. Two types of path are possible for electrons in the atom, circles and near-ellipses which rotate about one focus in the plane of the ellipse. The correspondence principle permits one to decide what stationary states are present or possible in a given atom. An essential feature of the theory is the high degree of interaction between electrons belonging to different groups. The normal He atom has both electrons in equiv. nearly circular paths of quant. nos.  $n_k = 1$ , whose planes lie at an angle of  $120^\circ$ , and which slowly turn around the fixed axis of angular momentum (cf. Kemble, C. A. 15, 2775). Calcns. of the ionization potential are still in progress. The "metastable" He atom has one of its electrons in a  $2l$  path. The Li atom has 2 electrons in  $1l$  paths like normal He, and the third in an eccentric  $2l$  ellipse which lies for the most part outside the  $1l$  circles, but partly within them. The 4th, 5th, and 6th electrons have similar paths, and in the C atom the normals to the planes of the 4 eccentric ellipses are the lines connecting the corners of a regular tetrahedron with its center. This seems to indicate the nature of the non-polar bond, but the question is

not further treated. The 7th electron (nitrogen) cannot have a  $2_1$  path. It takes, as do the 8th, 9th, and 10th, a circular course of type  $2_2$ . These circles lie outside the  $1_1$  circles, but partly within the  $2_1$  ellipses. In neon the planes of the four  $2_1$  paths have high spatial symmetry and also a harmonic configuration relative to the 4 elliptical  $2_2$  paths. The axis of (tetrahedral) symmetry of both groups coincides with the center of the innermost pair. Similar structures are described in detail for the first 21 elements, the rare gases, and a few others. The middle elements of the 4th, 5th and 6th periods form transition series in which an "inner" or lower-quant.-no. group is being completed instead of an overlying group. Thus in the 4th period the electrons take  $4_1$  paths until with Sc for the first time an "inner"  $3_1$  path is found to correspond to a firmer binding of the added electron. In these transition series the exact course of the process is lost from sight, but the lack of inner symmetry causes *paramagnetism of ions*, and the existence of different possible bindings of nearly equal firmness causes *variable valence and color of ions*. These properties are more marked in the 4th period than in the 5th, because electrons are more likely to leave their normal (external) paths for the  $3_1$  circles of the former period, than for the  $4_1$  ellipses of the latter. Similar reasons are proposed for the greater similarity of the 7th period to the 5th than to the 6th. *The spectra of Na* (in detail) and the other *alkalies*, the *Stark effect*, normal and abnormal, *Zeeman effects*, *intensity distribution in spectra*, *nature of X-ray absorption and emission phenomena*, increase of at. vol. within the alkali family, and other properties of the elements are treated from the same point of view. Mathematical details will be published.

NORRIS F. HALL

**Discussion on the structure of molecules.** *Rept. Brit. Assoc. Advancement Science 1921, 468-72.*—Symposium. I. LANGMUIR presented and discussed the 3 fundamental postulates of the Lewis-Langmuir theory, *viz.*, (1) the electrons in atoms or ions tend to surround the nucleus in successive layers contg. 2,8,8,18,18 and 32 electrons resp.; (2) 2 atoms may be coupled together by one or more duplets held in common by the completed sheaths of the atoms; and (3) the residual charge on each atom and on each group of atoms tends to a min. W. L. BRAGG considered the inadequacy of ordinary ideas of valency in light of X-ray analysis and showed that by recent measurements of the amplitudes of waves diffracted by Na and Cl the distribution of electrons in those atoms is very different from that pictured by the Langmuir theory, for there is a far greater d. of electrons near the center of the atom than in the outer region. The success of L.'s model in explaining complex compds. does not depend upon any assumption as to the exact structure of the atom, but on the fundamental conceptions of combination through electrostatic attraction and by electron sharing. J. R. PARTINGTON presented the following points: (1) translational and rotational energies are approx. represented by the theory of equipartition, and any excess of  $C_v$  above 6 is approx. parallel with the activities in non-polar gases; (2) translational energy on the basis of the quantum theory with the collision frequency  $\nu$  is 2.98 for all gases, but the  $\beta\nu$  values are of the same order as the observed values of  $C_v$ , and the rotational frequencies may be whole multiples of the translational; (3) the value of  $n$  in  $\eta = \eta_0 (T/273)^n$ , where  $\eta$  = viscosity, is related to the crit. pressure  $p_c$ , by  $n = 0.642 + 0.00116 p_c + 0.0000399 p_c^2$ ; (4) the mol. heat of H is not satisfactorily represented by Einstein's formula with  $\beta\nu = \text{const.}$  (Eucken), or  $\beta\nu \propto \sqrt{T}$  (Nernst), but it is by Debye's formula with  $\beta\nu = 65/\sqrt{T}$ ; (5) the model of the  $N_2$  mol. on Bohr's theory has the correct energy if 3 coplanar rings of 8, 4, and 2 electrons, between the 2 nuclei, are assumed, and  $\nu = A\omega/B \cos \phi$ , as in Krüger's theory. A. O. RANKINE cited evidence in support of the Lewis-Langmuir theory from the kinetic theory of gases. Thus the dimensions of the mol.  $Cl_2$  detd. from viscosity is that of 2 A atoms with contiguous outer shells and sharing electrons. Since the domains occupied by Rb and  $NH_4$  in crystals are almost identical, the same

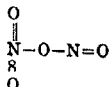
should be true of Kr and  $\text{CH}_4$  which have 1 positive charge and 1 electron less than Rb and  $\text{NH}_4$ , resp. The actual diams. are 3.10 and  $3.13 \times 10^{-8}$ , resp. S. H. C. BRIDGE extended the coordination theory to electrons and showed the convergence of this affinity theory and the older theory of valency. (Cf. C. A. 16, 17.) E. K. RIDGAL considered the difficulties of the static atom (structure of  $\text{N}_2$  mol., formation of cis- and trans-compds. in ethylenic series, and gradual transition from polar to unionized compds.), the difference in reactivity in an assemblage of mols. apparently alike, and the validity of the inverse-square law at sub-atomic distances. G. L. CLARE

A significant exception to the principle of selection. PAUL D. FOOT, F. L. MONLIER AND W. F. MEGGERS. *Phil. Mag.* 43, 659-61 (1922).—According to the Rubinowicz principle of selection (C. A. 13, 1415) the azimuthal quantum number, in any transition of an electron from one stationary orbit to another, resulting in radiation, may change only by +1, 0 or -1. Certain enhanced lines emitted by the ionized He atom indicate 2, which has been ascribed to the incipient Stark effect of the applied electrostatic field. In the present work the spectrum of K has been examd. with a new form of discharge tube in which the applied field can exert no influence on the radiation. The lines 1s-3d were observed to be very intense at 1000 while absent at 70 milli-amperes current. The azimuthal no. for these lines is 2 according to Sommerfeld, contrary to the Rubinowicz principle, and cannot be attributed to Stark effect. This suggests that the extra components in the fine structure of the He lines also may not be due to the applied field. The explanation may involve reconsideration of the assignment of single azimuthal nos. to each of the s, p, d and f terms. S. C. LUND

New mode of procedure for shattering atoms. H. ELBERTSHAGEN. *Z. Elektrochem.* 28, 118-9 (1922).—Shattering of atoms into their components might be accomplished by introducing a highly compressed monat. gas of high at. wt. (e. g., Hg, since the heavy atoms are less stable than the lighter) between the electrodes of a sparking device of the highest possible potential. H. JERMAIN CREIGHTON

The structure of chlorine dioxide and related compounds. G. A. PERKINS. *Philippine J. Sci.* 19, 729-40 (1922); cf. C. A. 16, 667.—P. discusses the possibility of the constituent atoms of a mol. contg. an odd number of electrons (e. g.,  $\text{ClO}_2$  with 19), being united by an odd number of electrons. Electrons can be shared only when an approx. equality exists between the electron binding strength of the two atoms. The variation of a given atom in this property is one of the consequences of the "electron shift" due to the proximity of a foreign charge. The partial removal of two or more electrons causes those remaining to be more closely bound to their nucleus. This strength increases with increase in covalence. Since the binding strength of univalent O is weak compared with that of F, no oxides are formed. Trivalent N and quadricovalent C, being more nearly equal strength, give ONF and  $\text{CH}_4$  resp. Univalent Cl, with its larger kernel, has greater binding strength than univalent O, though markedly less than univalent F or bivalent O. Therefore the formula for  $\text{Cl}_2\text{O}$  is probably Cl-Cl $\alpha$ O. That bi- or tri-covalent Cl does not form stable unions with univalent O may be due to the difference in size of their resp. kernels. Only quadricovalent Cl has sufficient binding strength to form a stable union with bivalent O ( $\text{Cl}_2\text{O}_2$ ). Therefore  $\text{ClO}_2$  contg. no bivalent O, is formed in reactions which should give unstable  $\text{Cl}_2\text{O}_2$  or  $\text{Cl}_2\text{O}_4$ . When an electron is removed from an O of the ion  $:\text{O}:\text{Cl}:\text{O}:$  forming the neutral mol., the vacancy in the O shell is filled by closer approach of the Cl shell, so that one more electron is shared by the two atoms:  $:\text{O}:\text{Cl}:\text{O}:$   $\text{ClO}_2$  m.  $-76^\circ$ , b.  $10^\circ$  mol. vol. is 45.  $\text{SO}_2$ ,  $:\ddot{\text{O}}:\ddot{\text{S}}:\ddot{\text{O}}:$ , m.  $-76^\circ$ , b.  $-10^\circ$ , mol. vol. 45. P. calls a 1-electron bond, a half bond, and suggests a new symbolism.  $\text{NO}_2$  is analogous to  $\text{Cl}_2$ ,  $\text{O} = \text{N} = \text{O}$ . Quadricovalent N has greater electron binding

strength than the trivalent Cl (in  $\text{Cl}_2\text{O}_4$ ) due to the smaller kernel and the displacement of electrons through the double bond. Therefore  $\text{NO}_2$  associates giving



In nitric oxide the 7 kernel electrons can be explained as two groups of 4 in which one electron is shared.

I. P. ROLF

The separation of isotopes by thermal and pressure diffusion. R. S. MULLIKEN. *J. Am. Chem. Soc.* 44, 1033-51 (1922); cf. *C. A.* 16, 1359.—Simple equations are developed giving the change in compn. and at. wt. of any mixt. of isotopes when subjected to thermal diffusion or to centrifuging. The former method is shown to be always less effective than the methods of irreversible evapn. or mol. diffusion. The same equations are demonstrated to apply to centrifuging of liquid or gaseous isotopic mixts. and in general of mixts. of any gases of not very unequal mol. wts. The degree of sepn. obtained in a given operation is found to be characteristic of each isotopic element regardless of its state of combination, and depends on the mol. fractions and differences of at. wt. of different isotopes, but not on the magnitude of the at. wt. itself. In this independence of at. and mol. wts. the method differs from evapn. and diffusion, and is thus relatively much more favorable than the latter for the heavier elements. The usefulness of the centrifugal method depends, however, on securing peripheral speeds approaching  $10^4$  cm./sec. A method of *evaporative centrifuging* for gases of moderate mol. wt. is proposed which approx. doubles the effect of a given centrifugal force. Expts. on the sepn. of liquid Hg by centrifuging are conclusively negative, due, as exptly. shown, to vibration of the centrifuge. A correction is made to the previous paper to the effect that the method of gaseous diffusion is probably less favorable than mol. diffusion for the sepn. of isotopes.

G. L. CLARK

The traces of  $\alpha$  particles upon a photographic plate. E. MÖHLESTEIN. *Arch. sci. phys. nat.* 4, 38-63 (1922).—M. discusses the previous work in this field, and includes a bibliography. He obtains halos of uniformly circular cross-section, by immersing a photographic plate impregnated with active material into mercury during the time of exposure. In halos from active deposit there were three distinct concentric regions: a solid center, probably the diam. of the active material, then a slightly lighter region due to  $\alpha$  particles from Ra A in addition to Ra C, and an outer circle marking the end of the range of  $\alpha$  particles from Ra C alone. The innermost section is in some cases a point. The diam. of the halo is in this case twice the range of the  $\alpha$  particle in the emulsion. The ranges of  $\alpha$  particles from Ra C and Po are 50.0 and 27.7 microns, resp. Their ratio, 1.81, is in good agreement with the ratio of their ranges in air. Calcns. indicate that every particle of AgBr lying in the path of an  $\alpha$  particle is reduced. Thus the no. of AgBr particles reduced is proportional to the length of path of the  $\alpha$  particle in the emulsion. This relation affords a means of getting the range in air by extrapolation, and also permits a photographic detn. of the no. of  $\alpha$  particles emitted from an active source.

D. C. BARDWELL

The number of radioactive transformations as determined by analysis of the observations. H. LEVY. *Proc. Phys. Soc. London* 34, 108-13 (1922).—A mathematical paper on finding a criterion for detg. the value of  $n$  in the radioactive transformation equation.

L. D. ROBERTS

The measurement of the radium content of sealed metal tubes. E. A. OWEN AND BERTHA NAYLOR. *Proc. Phys. Soc. London* 34, 92-7 (1922).—Pt and Ag tubes are considered when full of Ra salt and when almost empty. The correction equations

are worked out mathematically for both cases and proved exptly. Tables show corrections for the thickness of the walls.

L. D. ROSENBERG

**Hour radio activity of mineral waters. Carbonic-sulfur-boric waters of the Saturnia hot springs.** R. NASINI AND C. PORLEZZA. *Giorn. chim. ind. applicata* 3, 543-5(1921).—Frenkel defined radioactivity of the gases issuing from a spring as equal to the no. of mg. of RaBr<sub>3</sub> which, placed in 10 l. of air for a period of 1 min., charge the 10 l. of air with a quantity of emanation equal to that present in 10 l. of the natural gases of the spring. Hour radioactivity =  $P_s \times R/10$ , where  $P_s$  is the yield of gas expressed in l. per hr., and  $R$  the value of radioactivity as defined above. N. and P. apply the definition also to the waters of a spring. They obtained a value for the hour radioactivity of the waters of the Saturnia hot-springs of 0.137 millicurie. Three tables are appended: (I) Fixed residue, physicochem. const. and dissolved gases; (II) substances dissolved in 1 l. of the mineral waters expressed in ions; (III) most probable compn. on the basis of modern physicochem. theories. ROBERT S. POSMONTIER

**Experiments on distribution of active deposit from radium emanation under the action of an electric field.** WALTER MUND. *J. phys. radium* 2, 378-83(1921).—Two metallic plates 180 mm. in diam. are clamped against a rubber ring, sepg. them 35 mm. In the center of each plate a circular section of 70 mm. diam. is cut out, into which is threaded a disk. One plate is grounded and the other connected to the negative pole of a battery giving p. d.'s up to 1800 v. The chamber, previously charged with a definite p. d. is evacuated and a 24-hr. accumulation of Ra Em from  $2.67 \times 10^{-4}$  g. Ra introduced. The Em is allowed to remain 20 min. and is then pumped out. The detachable disks are removed and placed under 2 gold-leaf electrosopes. After 20 min. the time of fall is read simultaneously on both instruments.  $U_1$  is the time (corrected for natural leak) for the grounded plate;  $U_2$  is the same for the negatively charged plate.  $C = U_1/U_2$  for a zero p. d. Let  $R = U_2/CU_1$  and  $D = 20(R-1)/(R+1)$ . For voltages varying from 0 to 1800,  $D$  varies from zero to 17.68. Plotting  $D$  as ordinates and  $V$  as abscissas, a curve is obtained very similar to the curve of current against voltage in an ionized gas from zero to satn. current. Before a theoretical explanation is proposed, M. suggests that a more complete study be made, with the varying pressure and kind of gas, and amounts of Em used. D. C. BARDWELL

**Invariability of radioactivity in strong magnetic fields.** A. PICCARD AND G. VOLKART. *Arch. sci. phys. nat.* 3, 543-4(1921); *Science Abstracts* 25A, 125-6.—Using magnetic fields of the order of 83,000 gauss for a period of 20 to 30 hrs., the authors have shown that the rate of decay of ThB is unaffected—any variation produced must be less than 1 part in 1000. H. G.

**Origin of uranium-Z<sub>1</sub> (Uranium-Z).** M. C. NEUBURGER. *Naturwissenschaften* 9, 235-6(1921).—Supplementary to the work of Hahn (cf. C. A. 15, 3026), N. describes 3 possible types of disintegration in the Ra-U series to account for the occurrence of the newly discovered U-Z. The existence of 2 new elements thereby follows, namely, U III in Group VI, giving  $\alpha$ -rays, and U-Z in Group IV, giving  $\beta$ -rays. Besides the transformations due to the emission of ordinary  $\alpha$ -rays, there are others due to Rutherford's He isotope,  $X_1$ , which are termed iso- $\alpha$ -particles. J. C. S.

**Origin of Uranium-Z.** OTTO HAHN. *Naturwissenschaften* 9, 236(1921).—H. rejects the possibility of the transformations suggested by Neuburger (preceding abst.) as improbable and lacking exptl. foundation. J. C. S.

**Halos and earth history: a new radioactive element.** J. JOLY. *Nature* 109, 517-8, 578-9(1922).—An account is given of very small, colorless, spherical, halo-like forms occurring in the Archaean black mica of Ytterby. The greater number of these halos are remarkably uniform in size and have an av. radius of 0.0052  $\mu$ . These haloes may be due to a radioactive element emitting  $\alpha$ -rays of a range in air of 1 to 1.5

cm. No evidence of its further disintegration has been found. The name "hibernium" is suggested. W. H. ROSS

**Determining the radium content of carnotite ores and other products of low activity.** V. F. HESS. *Trans. Am. Electrochem. Soc.* 41 (Preprint No. 19, Apr., 1922).—The sample is hermetically sealed in a cubical wooden container having a recess which allows the  $\gamma$ -ray electrometer to be introduced into the center and thus be practically surrounded by the sample. From the observed discharge the Ra content of the sample is calcd. directly by means of certain consts. The method, described in detail, is suitable for ores contg. between  $10^{-10}$  and  $10^{-2}$  g. Ra per g. of material. C. C. V. V.

**Application of the electron theory of chemistry to solids.** J. J. THOMSON. *Phil. Mag.* 43, 721-57(1922).—A theory of the structure of solids is given based on the views previously given by T. (C. A. 14, 3570; 15, 1651) as to the nature of the structure of atoms and the mechanism of chem. combination. Since the atom of a univalent element has one disposable electron, that of a bivalent 2, etc., there must be in the crystal of a univalent element such an arrangement of electrons and atoms that for each atom there is one electron, in a crystal of a bivalent atom there must be two electrons for each atom, etc. It is shown that this condition detcs. the crystallographic forms in which the various elements can crystallize, and leads to a conception of the structure of cryst. solids which allows the calcn. without further assumptions of certain phys. consts. such as the bulk modulus, the crit. frequency, and the dielec. const. The values of these calcd. for elements of different valencies agree closely with the exptl. values.

S. C. L.

**The red limit and spectral distribution of the photoelectric emission of platinum as affected by its gas content.** RUDOLF SUHRMANN. *Ann. Physik* 67, 43-68(1922).—The app. is a cell contg. a strip of Pt foil so mounted on leads that it can be heated electrically. The foil is opposite a quartz window which admits light from a quartz-mercury lamp after dispersion through an ultraviolet monochromator. Before it enters the cell the intensity of each ray may be measured with a thermocouple suitably arranged. The photoelec. emission of a metal is affected not only by the gas it has absorbed but also by the gaseous layer adsorbed on it. The effect of the adsorbed gas is to retard electron emission, while the absorbed gases promote it. The exptl. work consisted of the measurement of the photoelec. emission of the Pt foil when exposed to the various rays of the Hg lamp, the gas content of the foil being changed by repeatedly heating it, first to red heat, then to white heat. After each heating all gases were removed from the cell by pumping. The range of spectrum extended from  $217\mu$  to  $334\mu$ . The following facts were established: (1).—The max. wave length capable of exciting electron emission increases from  $260\mu$  to  $300\mu$  for Pt from which the adsorbed gas has been removed. As the absorbed gases are driven off the red limit shifts again to shorter wave lengths until it reaches a point near  $270\mu$ . The red limit is defined quant. as that wave length for which the sp. photoelec. emission is less than  $1/1000$  of the highest observed value. There is no abs. red limit. (2).—The decrease in intensity of the electron emission for different wave lengths is markedly affected by the gas content of the Pt, the effect being most pronounced for the longer rays and least for the shorter rays. There is a region in the extreme ultraviolet portion of the spectrum, which the data indicate to be near  $150\mu$ , where the photoelec. emission of Pt metal, free from all gas, is comparable with that of the gas itself. C. C. KIESS

**The fine structure of the Balmer series.** ORTO OLDENBERG. *Ann. Physik* 67, 69-72(1922).—O., repeats the expts. of McLennan and Lowe (C. A. 16, 684), and finds that their conclusions that the H lines display a structure different from that required by Sommerfeld's theory are not justified. C. C. KIESS

**The growth and decay of photo-thermionic currents from oxide-coated filaments.**

H. D. ARNOLD AND H. E. IVRS. *Proc. Nat. Acad. Sci.* 7, 323-5(1921).—It had been found by Case (*C. A.* 15, 2782) and Merritt that when oxide-coated filaments of audion tubes were illuminated by light of short wave lengths the thermionic current was increased. This was considered to be a photoelec. action of the oxide-coated filament. The increase of this so-called photoelec. current as the temp. of the filament was increased was very marked, and such an increase of photoelec. emission with the temp. has not been found for the true photoelec. effect. The authors investigated this by illuminating the oxide-coated filaments of audion tubes with red and blue light, and recording the growth and decay of the added currents caused by the light. The effect due to the red light was caused by an increased heating of the filament; for the shape of the growth and decay curves as well as their change with the temp. of the filament was very similar to that produced by a small increment in the heating current in the filament. With the blue light the heating effect was absent. The blue light produced a current which at low filament temps. rose to its max. slowly after illumination began. On removal of the light the decay of the current was also slow. As the temp. of the filament increased the max. value of the currents caused by illumination at first increased and later decreased. With increasing filament temp. the response of the current to the illumination became very rapid. These effects indicated some sort of a photoelec. emission. Since (no matter what the temp.), a true photoelec. effect sets in instantaneously with the illumination, the above effect is not a true photoelec. effect according to A. and I., who propose the name "photo-thermionic emission" to describe it. The shape of the growth and decay curves and the changes of these curves with temp. indicate a possible similarity to the light-sensitive response of Se. L. B. LOGS

The systematization of X-ray spectra. G. WENTZEL. *Z. Physik* 6, 84-99(1921).—In this paper X-ray spectra are for the first time systematized in two respects, (1) the grouping of the "energy-levels" (Niveau) concerned in characteristic X-ray production, (2) the actual X-ray lines produced, as governed by certain "Selective Principles." It is shown that there are 1 K-level, 3 L-levels, 5 M, and 7 N. Adjacent levels form pairs of two types, regular and irregular, in such a manner that these two kinds alternate. A regular doublet is characterized by an approx. const. wave length sepn., and Sommerfeld has shown that this sepn. may be quant. explained by the assumption of circular and elliptic electron orbits, using the relativity variation of mass with velocity. A regular doublet is thus in a sense a "relativity" doublet since the doublet sepn. would be zero, if electron mass were const. The irregular doublets, on the other hand, are characterized by an approx. const. sepn. in the square root of frequency. In order to account for these irregular doublets it is necessary to introduce, besides the usual angular and radial quant numbers concerned in a plane elliptic path, a third arbitrary quant number, called the "Fundamental" quant number  $m$ . This remains const. for the two levels of a regular doublet, but its variation, by one unit, causes the irregular doublets. For the angular quant number  $n$ , the relations are reversed, since  $n$  remains const. for an irregular doublet but changes by one unit for a regular doublet. A study of the actual X-ray lines indicates a rational set of values for  $m$ , such that a selective principle holds for it also, i. e.,  $m$  may change in value by one unit only, during an electron transition. The selective principle of Rubinowicz as applied to  $n$  states that this may remain const. or change by one unit. The above principles enable the author to account quant. for all X-ray lines except possibly two or three very faint L lines found only in W, and certain K lines found only in light elements. R. T. BERGE

Regular and irregular doublets. A. SOMMERFELD AND G. WENTZEL. *Z. Physik* 7, 89-93(1921).—Quant. relations for regular doublets (see preceding abstr.) have been tested previously only for the  $L_1L_1$  and the  $M_1M_2$  pairs. These pairs exhibit to a high degree of accuracy the relativity sepn., as shown by the constancy, for all elements,

of the one undetd. const. appearing in the theoretical equations. This const. (the "screening" const.) gives the amt. by which the true nuclear charge must be decreased, in order to obtain the "effective" nuclear charge. S. and W. now test other regular doublets and obtain values for this const. The results are entirely satisfactory, the values for different doublets increasing in a rational manner, as one goes to the outer energy levels. It is further found that the irregular doublets may be ascribed to a *change* in this screening const., i. e., while a regular doublet is caused by a change in the *form* of the electron path, the effective nuclear charge remaining const., an irregular doublet is caused by a change in the effective nuclear charge, the form of the path remaining const. The *change* in this charge, as computed from the various irregular doublets, agrees only qual. with the various *actual* values of the charge, as computed from the regular doublets, indicating that the above assumptions are only a first approximation.

R. T. BIRGE

The systematization of X-ray spectra. D. COSTER. *Z. Physik* 6, 185-203 (1921).—This article is a continuation of previous exptl. and theoretical work by C. on the L series of the heavy elements (*C. A.* 15, 1855, 2786). With the use of a metal X-ray tube, a new search has been made for very weak lines. The chief difficulty arises from the presence of large numbers of impurity lines, but in spite of this certain new lines, notably a  $\beta_3$  line, were identified and measured. Complete tables of all of the author's measurements, new and old, are given. The major portion of the article is concerned with the quant. relations between the lines themselves and the various energy levels. [NOTE BY ABSTRACTOR:—This work was done independently of that by Wentzel, (see second preceding abstract,) and very many of the conclusions, especially in regard to the allocation of the lines to the various levels, agree with those of Wentzel. The set of energy levels deduced agrees with Wentzel's, but the interrelations are not as complete. Thus Coster labels the levels either *a* or *b* in such a way that transitions *a* to *a*, or *b* to *b* never occur. This is equivalent to Wentzel's second selective principle, for such transitions correspond to a change of zero or two units in Wentzel's "Grund" quant. number. Finally, all regular doublets are studied, rough values of the screening const. computed, and these values discussed theoretically. These computations are in advance of Sommerfeld and Wentzel's work, (see preceding abstract).]

R. T. BIRGE

A contribution to the knowledge of X-ray spectra. E. HJALMAR. *Z. Physik* 7, 341-50 (1921).—(1) The  $K\beta$  line of S is shown to be double, by means of photometric curves and ordinary photographs, and the new component has apparently the theoretical position of  $K_{\gamma}$ , as deduced from the position of  $K_{\gamma}$  in other elements. This result is of importance since the fourth electron layer—the supposed initial layer for  $K_{\gamma}$ —does not begin to form until K is reached. (2) An attempt is made to investigate the effect of valency on the frequency of the S K-lines, but the exptl. difficulties prove too great. Lindh has found such an effect for Cl. (3) A few new precision measurements of S, Cl, K, and Zn K-lines are listed. (4) A slight error has been found affecting all of H.'s previous L-series measurements (*C. A.* 15, 1101) from  $Z=52$  on. A complete table is given of all of H.'s L-series measurements, including all new and corrected values.

R. T. BIRGE

The penetrating radiation and its bearing upon the earth's electric field. W. F. G. SWANN. *Bull. Nat. Res. Council* 3, Pt. 2, No. 17, 65-73 (1922).—Investigations on penetrating radiation in progress at the Univ. of Minn. are described. In a hermetically sealed Zn vessel freed from radioactive air 8 or 9 ions per cc. per sec. are produced. Of this no. 0.06 is normal  $\gamma$ -ray radiation from the atm., 1.6 from the soil and 0.8 from sec. ionization, leaving 6 ions per cc. per sec. due to radiation which may penetrate an appreciable layer of  $H_2O$ . Preliminary expts. on the variation of residual ionization



with pressure indicate that of the ionization at atm. pressure and ordinarily attributed to penetrating radiation much less than 1 ion per cc. per sec. is to be accounted for as having its origin in a direct action of the primary radiation in the gas or an emitted secondary radiation. Expts. with special app. on the direction of the penetrating radiation showed an excess coming from above. The earth's charge is postulated as that in which the expulsion of the electrons from the atoms of air is brought about by the penetrating radiation from above, the hard nature of which results in emission of electrons from air mols. almost exclusively in the downward direction. A penetrating range of 9 meters is sufficient then to account for the earth's charge. G. L. CLARK

**Influence of Röntgen rays on the catalysis of hydrogen peroxide by platinum.** R. SCHWARTZ AND W. FRIEDRICH. *Ber.* 55B, 1040-51 (1922).—The action of X-rays on the decompn. of 30%  $H_2O_2$  by Pt sol. and by catalase has been studied at room temp. In some of the expts. both the  $H_2O_2$  and the catalyst were subjected to the action of the rays; in others only the catalyst. The effect of the radiation is to decrease the rate of decompn., and to give to the time-log  $[a/(a-x)]$  curve a concave bend.

H. JERMAIN CREIGHTON

**The distortive effect of the spectrometer crystal on the continuous Röntgen spectrum.** HANS KÜSTNER. *Z. Physik* 7, 97-110 (1921).—The observed intensities at various wave lengths in the continuous X-ray spectrum are affected by errors attributable to the crystal used in the spectrometer, and introduced by one or more of the following causes: (1) The atoms of the crystal may have absorption bands for the radiation falling in the region to be observed; (2) at the glancing angle,  $\varphi$ , rays of various wave lengths in overlapping orders are superposed on the continuous spectrum to be measured; (3) the reflecting power of the crystal at the angle  $\varphi$  is a function of the wave length and also of the order of spectrum and is expressed as  $R = I/E = f(\lambda, n)$  where  $E$  and  $I$  are the incident and reflected intensities, resp. and  $\lambda$  and  $n$  represent wave length and order of spectrum; (4) as a result of its temp. the atoms of the crystal scatter a small amt. of radiation; but only a very small portion of it is observed in the ionization chamber. A proper choice of crystal will eliminate the first of these sources of error, and allowances can be made for the second from a knowledge of its properties. The value of  $R$  can be measured for any crystal for any wave length, but the form and influence of  $f(\lambda, n)$  have not hitherto been investigated. From theoretical considerations Bragg has derived an expression for  $R$  which he applied to his observations with rock salt at  $\lambda = 0.615\text{\AA}$ . The author modifies Bragg's equation to make it applicable in finding  $R$  for other wave lengths, and applies his results to the data of Behnken for rock salt and to those of Ulrey for calcite. While no claim to great accuracy is made, yet the results indicate that when observed intensity curves are corrected for the distortive effect of the crystal used, the region of maximum intensity is shifted in the direction of longer wave lengths, and that there are also changes in the form and course of the intensity curve. In order to obtain the true curve of intensities in the continuous spectrum the crystal employed should have its reflecting power measured for all wave lengths and orders of spectrum falling in the region examd. C. C. KRSS.

**Determination of crystal structures by means of X-rays.** M. VON LAUE. *Naturwissenschaften* 8, 968-71 (1920).—A theoretical discussion showing the limitations of the X-ray method for the detn. of crystal structures. The lattice image is not a refraction, but an interference, image. Information as to crystal structure is actually obtained by considering the results obtained with rays falling at different angles and of different wave lengths. Additional information is given by chem. constitution, the dispersive power of the atoms present for the rays used, crystal form, and the mathematical theory of simple and compd. space lattices. J. C. S.

**X-rays and thermodynamic equilibrium.** L. DE BROGLIE. *J. phys. radium* 3,

33-45(1922).—A purely mathematical discussion on a thermodynamic basis of the atomic absorption of X-ray energy. No chem. applications and no exptl. results are given.

E. D. WILLIAMSON

Röntgen spectra and chemical valence. GREGOR WENTZEL. *Naturwissenschaften* 10, 464-8(1922).—A discussion of the dependence of the K absorption limits of Cl and P upon the valence as observed by Lindh (cf. *C. A.* 15, 3586) and Bergengren (*C. A.* 15, 207). It is probable that the properties of the K limits of Ti, V and Cr reported by Fricke (cf. *C. A.* 14, 3363) are due in so far as this structure extends to the weaker part to the presence of ions of different valence. The structure of the K- $\beta$  line of the light elements is explained similarly (cf. *C. A.* 15, 2245).

C. C. DAVIS

Wave propagation in optically heterogeneous media. Christiansen's experiment. N. K. SETHI. *Proc. Indian Assoc. for Cultivation of Science* 6, Pts. 3 and 4, 121-41 (1921); *Science Abstracts* 24A, 810-1; cf. *C. A.* 15, 985.—This paper describes the results of a detailed study, both exptl. and theoretical, which has been made of the phenomena observed in Christiansen's expt. in which the powder of a transparent substance is immersed in a mixt. of  $\text{CS}_2$  and  $\text{C}_6\text{H}_6$  having a  $n$  nearly equal to that of the powder. *Transmitted light.*—The range of wave lengths transmitted by the mixt. has been found to depend on the intensity of the incident light. A theoretical treatment based on the principles of the wave-theory and the theory of probability is given, and shows that the intensity of the transmitted light is given by the expression  $I = I_0 \exp -cd((\mu - \mu')/\lambda)^2$ , where  $c$  is a const. which has been found roughly equal to 7,  $t$  is the thickness of the layer of powder,  $d$  the size of the particles, and  $\mu$  and  $\mu'$  are the  $n$ 's of the two components of the mixt. The formula shows that with the very finest powders the range of transmission may be very considerable. *Colors of the halo.*—The statement made hitherto that the color of the halo is complementary to that of the transmitted light is not correct. The halo is not of one color throughout, but has a definite structure. This is shown by observations and photographs of the spectrum of the halo, which at small obliquities consists of two narrow bright bands sep'd. by a dark interval; these bands widen out as the angle of observation is increased. The facts are explained by observations in monochromatic light which indicate that the distribution of intensity in the halo may be taken to be of the form  $e \exp -bx^2/(\mu - \mu')^2$ , where  $b$  increases as the size of the particles is increased and as the thickness of the layer or the wave length of light is diminished. *Surface colors.*—The level surface of sep'n. between the clear liquid on the top and the powder below exhibits brilliant colors which are not only different at different stages of the mixt. as regards the reflective indices, but are also different on the two sides of the boundary. This effect does not appear to have been noticed before. Presumably it is due to total reflection effects at the boundary. *Liquid mixtures.*—A mixt. of glycerol and turpentine shows similar phenomena, but these become evident only when the flask contg. the mixt. is heated by immersion in hot water. At ordinary temps. there is no light transmitted. The halo in this case is, however, much smaller, but the general transparency of the mixt. is very great. Some interesting diffraction effects by the edges of the liquid drops were observed. *Colors of doubly refracting powders.*—Doubly refracting powders, such as quartz, are, contrary to the statement of R. W. Wood, unsuitable for the exhibition of the true Christiansen phenomenon, because in their case there is no regularly transmitted light. The whole of the light emerging through the powder appears in the halo, which is differently colored in parts. There is a particular wave length for which the size of the halo is a min., and this has been shown both theoretically and experimentally to correspond to the case in which the  $n$  of the liquid is equal to  $\frac{1}{2}(\mu_0 + \frac{1}{2}(\mu_0 + \mu_1))$ , where  $\mu_0$  and  $\mu_1$  are, resp., the  $n$ s for the ordinary and extraordinary rays. H. G.

The kinetic theory of absorption in gases (absorption spectra). G. RIBAUD.

*J. phys. radium* 3, 81-6(1922).—On the basis of the theory that the energy absorbed by an electron from light waves increases the kinetic energy of the mol. contg. the electron, the energy taken up by an absorbing mol. is calcd. The total energy absorbed per sec. by a certain no. of absorbing mols. is independent of the pressure. The mean energy absorbed per sec. from radiant energy under the most favorable conditions by a mol. is calcd. to be  $4 \times 10^{-9}$  ergs, which is  $10^8$  times the kinetic energy of a mol. at ordinary temp. Absorption of energy is assumed to take place continuously and not in quanta. In the case of fluorescent gases, when a quantum is accumulated, instead of being dissipated as heat, it is emitted again as light. E. N. BUNTING

Minimum electron energies associated with the excitation of the spectra of helium. ANN C. DAVIS. *Proc. Roy. Soc. (London)* 100A, 599-620(1922).—These expts. were made to det. the min. voltages at which lines of the ordinary serial systems, lines of the enhanced system, and lines of the band spectrum of He could be obtained under different conditions of gas pressure and electron current density with a view to testing whether the assoc. of the band spectrum with the  $He_2$  mol. can be reconciled with the recent suggestions as to the production of this mol.; and also with a view to testing the possibility of exciting lines in the He spectrum, other than the single line, without ionization occurring. Two forms of app. were used, one of which was specially designed with a view to detecting differences in the voltages required for the stimulation of different lines, and the other to obtain low-voltage arcs. The first appearance of the different spectral lines was investigated both visually and photographically. The results indicate that the occurrence of ionization of the He atom is essential for the production of any of the ortho-He or par-He lines. Whenever members of these series are observed below the min. ionizing voltage 25.2 volts, ionization of the He by cumulative effects must occur. With increase in electron current ionization by successive collisions increases so that after once being excited, spectrum lines can be maintained while the potential is reduced to 13 v. or less. Under different sets of conditions, 3 distinct limits were found for the min. voltage at which the enhanced line 4686 Å. could be obtained. About 80 v. was the limit at which this line could be detected when the pressure of He was 1 or 2 mm. With intense electron streams at these pressures 4686 Å. could be detected down to 54.2 v. At higher pressures intense electron streams stimulated this line at 50.8 volts but attempts to see it below this voltage were unsuccessful. It appears that the production of 4686 Å. between these lower limits does not result from the removal of the remaining electron in a positively charged He atom as the result of cumulative effects, but from single electron impacts on He positive ions without further ionization. Under no circumstances was the band spectrum of He seen without the presence of ortho- and par-He series, and the only limit which can be definitely assoc. with the He band spectrum is the min. radiation voltage, 20.4, since it has not been found possible to excite this spectrum at a lower voltage. The conditions under which this band spectrum made its appearance, and those under which it could be maintained, support the view that it has its origin in a He mol. which is produced from abnormal He atoms and thus that it cannot be produced in normal He for electron energies below 20.4 v. The results of the present investigation considered in conjunction with the conclusion that at 20.4 volts some system is produced in He which can be ionized by the radiation produced at 21.2 v. (a second radiation potential) support the suggestion that the coplanar ats. resulting from 20.4 v. electron collisions with He ats. are capable of forming  $He_2$  mols. from which the band spectrum arises. W. F. MCGOWAN

Series regularities in the resonance spectrum of iodine. R. MECKE. *Z. Physik* 7, 73-85(1921).—The resonance spectrum of I consists of groups each composed of 8 or 10 lines. Wood has given measurements of the different resonance spectra excited by the green and the two yellow Hg lines; that excited by the green line was most thor-

oroughly studied (C. A. 12, 1148). The lines composing each group are homologous members of related series. Each series is given by the formula  $\nu = A + Bm + Cm^2 + Dm^3$ , where  $A$  is the wave number of the radiation which excites the resonance spectrum. The coeffs.  $C$  and  $D$  are the same for all the resonance spectra of I, no matter what the wave length of the exciting radiation is. The coeff.  $B$ , however, varies with the series; but it is of the form  $B = b_0 - b_1n$ , where  $n$  takes on integral values from 0 to 3. Each line of every series thus represented is itself double. The family of series given by the above formula is composed of a fundamental series  $\nu_0 = F(m)$  and two groups each of four related series found by adding to or subtracting from  $F(m)$  certain values,  $\Delta\nu$ , depending on the coeff.  $B$ . Theoretical considerations indicate that the number  $m$  represents an azimuthal quantum number. Assuming that the moment of inertia is attributable to a rotating ring of electrons rather than to a rotation of the mol. itself, it is possible to express the above series formula as a difference of energy terms. This would therefore ascribe the resonance spectrum, as well as the line spectrum, to the interorbital movements of electrons.

C. C. KRESS

The deviation from Stokes' law in the excitation of iodine vapor fluorescence. PETER PRINGSHEIM. *Z. Physik* 7, 203-16(1921).—The empirical Stokes law that the wave length of fluorescence radiation is always greater than that of the exciting light appeared to be a necessary consequence of the quantum theory since not more than one quantum of the same magnitude as was absorbed could be emitted by the same resonator. In fact, however, there exist many exceptions to Stokes' rule. Although the center of gravity of the exciting energy is always of shorter wave length than that of the fluorescent band, these two spectral regions often overlap and in such cases the entire fluorescent band can be produced by light whose wave length is greater than the lower limit of the emission band. In such cases part of the secondary radiation is of higher frequency than the primary, i. e., greater quanta are emitted than are absorbed. Einstein suggested that this must be accounted for by transfer of heat energy of the radiating mols. These expts. on I vapor were undertaken to test quant. the effect of temp. on the deviations from Stokes' law. The vapor was excited to fluorescence by illumination with the green radiation  $546.1\mu$  from a hot Hg arc lamp and the spectrum was photographed with 48-hour exposures, first when the vapor was at  $20^\circ$  and then at  $320^\circ$ . Microphotometer curves of the spectrograms showing 20 positive lines and four of negative order ("anti-Stokes" members whose wave lengths  $540, 534, 528$  (?) and  $523\mu$  are less than that of the exciting light  $546.1\mu$ ) are reproduced. The intensity of the negative terms is increased many fold when the temp. rises to  $320^\circ$ . Simultaneously a few of the positive terms (nos. 2, 7, 9, 14) increase in strength while most of them diminish in brightness. These resonance bands are in reality due to 7 close I lines covered by the relatively wide Hg line. The fine structure of the bands is not resolved and their different behavior is probably due to connection with series originating in different ones of the 7 I lines. It is established that deviations from Stokes' law increase with rising temp., and a possible explanation of this result is suggested.

W. F. MEGGERS

Catalysis. XV. Absorption spectra of triethylsulfonium bromide in various solvents, in the short infra-red region. H. A. TAYLOR AND WM. C. McC. LEWIS. *J. Chem. Soc.* 121, 665-75(1922).—The simplest formulation of the radiation hypothesis of ordinary or thermal reactions assumes that chemical change is due to a specific frequency of radiation characteristic of the substance involved, and it has been shown (Lewis, C. A. 11, 112) that one quantum of energy is necessary to decompose or activate a single mol. Thus it is possible to calc. the activating frequency or wave length from numerical values of critical increments obtained directly from measurement of the temp. coeffs. of velocity consts. Such calcs. show that for the majority of reactions

this lies in the short infra-red, and quant. verification of the theory is now given by a study of the decompn. of  $\text{Et}_2\text{SBr}$ , the kinetics of which had been previously measured by von Halban (*C. A.* 3, 2892) at various temps. and in various solvents. By means of a Hilger infra-red spectrometer and radiomicrometer, the absorption spectra of  $\text{Et}_2\text{SBr}$  is measured over the range  $0.7\mu$  to  $3.6\mu$  in 8 solvents, viz.:  $\text{C}_6\text{H}_5\text{NO}_2$ ,  $\text{C}_6\text{H}_5\text{Cl}$ , Pr alc., amyl alc., benzyl alc.,  $\text{AcOH}$ ,  $(\text{CH}_3)_2\text{CO}$  and  $\text{CHCl}_3$ . In each case the position which the absorption should occupy is calcd. from the critical increments of the reaction in the various solvents as derived from velocity-const. data and in the order named the absorption bands should have the wave lengths 1.0, 0.91, 0.84, 0.85, 0.78, 0.97, 0.90 and  $0.85\mu$ , while the corresponding observed values were 1.05, 0.90, 0.89, 0.83, 0.80, 0.93, 1.3 and  $1.0\mu$ . The agreement is considered satisfactory for the first 6 solvents, but not for acetone and  $\text{CHCl}_3$  in which cases, however, the velocity consts. are unsatisfactory and it is possible that the observed absorption here gives more trustworthy information of the reactivity of the solute than is given by the observed velocity "constants." In the case of  $\text{CHCl}_3$ , it is concluded that the polymerized form of the solute does not decompose directly into alkyl bromide and dialkyl bromide, but depolymerizes before decompn. becomes possible.

W. F. MCGGERS

**Infra-red frequencies of selenates and chromates.** CLEMENS SCHAEFER AND MARTHA SCHUBERT. *Z. Physik* 7, 297-308(1921).—In previous work (*C. A.* 11, 913) the infra-red frequencies of carbonates, sulfates, nitrates and the behavior of water of crystn. were investigated in the wave-length interval 1 to  $20\mu$ . The results of a similar investigation on selenates are now given. The reflecting powers of 6 selenates, an isomorphous mixt. of 2 selenates and 6 double selenates were measured both for unpolarized and for polarized light. Only one each of these types of chromates was studied. Reflection max. corresponding to natural frequencies of the metal atoms were found at about  $11.4\mu$  for selenates and at  $11.3\mu$  for chromates. These resemble the frequency at  $9\mu$  found for sulfates. Measurements with polarized light indicate that these reflection maxima are resolved by a uniaxial crystal into two, by a biaxial crystal into 3 groups of natural frequencies each of which is ascribed to a definite vibration direction in the crystal. No simple relation between natural frequency and at. mass is apparent and it is suspected that the max. due to the  $\text{CrO}_4$  group is for special reasons shifted to longer waves than would be expected from mass comparisons.

W. F. MCGGERS

**Infra-red frequencies of chlorates, bromates and iodates.** CLEMENS SCHAEFER AND MARTHA SCHUBERT. *Z. Physik* 7, 309-12(1921).—Results resembling those obtained for carbonates and nitrates (*C. A.* 13, 1559) represent the natural frequencies for chlorates, bromates and iodates. The first max. of reflection from chlorates is at about  $10.5\mu$ , from bromates at about  $12\mu$  and from iodates at  $12.5\mu$ . Indications of second maxima were also obtained but they appear to be abnormally displaced toward longer waves. For the chlorates they are at about  $16\mu$  while for the remainder they are beyond  $20\mu$ , the limit of observation.

W. F. MCGGERS

**Infra-red reflecting power of silica.** CLEMENS SCHAEFER AND MARTHA SCHUBERT. *Z. Physik* 7, 313-5(1921).—Curves of percentage reflection are given for 6 varieties of  $\text{SiO}_2$  in the wave-length interval 1 to  $22\mu$ . Cryst. quartz and micro-cryst. forms (chrysoprase, chalcedony, etc.) show the well known metallic reflection of 80 to 90% at about  $9\mu$ . Amorphous varieties (opal and fused quartz) also show max. reflection at  $9\mu$  but the band is narrower and is reduced to 40-50%. These differences must be explained by the destruction of the crystal space lattice.

W. F. MCGGERS

**Corpuscular spectra of the elements.** MAURICE DE BROGLIE. *Compt. rend.* 174, 939-41(1922).—A schematic representation of the corpuscular spectra of Ag, Sn, At and U as excited by 4 lines of the K series of W from a Coolidge tube. The details

are promised in a future publication. A continuous spectrum due to  $\beta$  rays is detected and evidence is obtained that the absorption of corpuscles by matter must be selective to a certain degree.

W. F. MEGGERS

The rare earths. XI. The arc spectrum of yttrium. L. F. YNTEMA with B. S. HOWANS. *J. Opt. Soc. Am. Rev. Sci. Inst.* 6, 121-34(1922).—The Y material prepd. at the Univ. of Ill. under direction of one of the authors (C. A. 10, 3006) has been used for investigating the arc spectrum of Y in the violet and ultra-violet regions. For this purpose a quartz-prism spectrograph was used. The wave lengths given in the table are the means of four detns. referred to the Fe arc spectrum as standard. They are given in international units and extend from  $\lambda = 2243 \text{ \AA.}$  to  $\lambda = 4188 \text{ \AA.}$  Rare-earth impurities present are Ho, Dy and Er, betrayed faintly only by their most prominent lines. Eder's results for the same region (C. A. 11, 1081) are given for comparison. It is to be noted that each list contains many faint lines not present in the other.

C. C. KIRSS

Absorption spectra of triphenylmethane dyes. E. ADINOLFI. *Rend. accad. sci. Napoli* [3] 27, 242-7(1921); *Science Abstracts* 25A, 123.—Examm. of the absorption spectra of a number of triphenylmethane dyes dissolved in various solvents shows that, starting from aq. solns., the halochromy exhibited by compds. of this series becomes increasingly marked as the mol. wt. of the solvent increases. Kundt's law, according to which the absorption bands are displaced towards the red end of the spectrum on passing from one solvent to another more highly refractive, is not applicable to the triphenylmethane group, the displacements being greater for ether than for EtOH and greater for benzene than for toluene.

H. G.

The luminescence of incandescent solids. E. L. NICHOLS and H. L. HOWES. *Phys. Rev.* 19, 300-18(1922).—Some oxides when heated to a temp. lying within a definite and sometimes narrow range, emit radiation in a limited region of the spectrum far in excess of the radiation emitted in that region by a black body at the same temp. This was observed with the oxides of Be, Mg, Ca, Zn, Al, Si, Zr, Ti, Sn, Gd, Ge, Er, Cb, Ce, Pr, and Nd. As a striking example the blue radiation from  $\text{Cb}_2\text{O}_3$  at  $560^\circ$  is 85,000 times the corresponding radiation from a black body, the ratio decreasing with increasing temp. until it is 1.35 at  $1037^\circ$ . The luminescence is different from temp. radiation not only in its variation with temp. and its spectrum distribution but also in showing fatigue effects and in varying with the previous heat treatment and with the method of heating. The luminescence is probably a phenomenon of instability associated with a chem. change such as oxidation or with the phys. disturbance which the oxides undergo as they are heated.

HARRY B. WEISER

Dispersion formulas and the polarization of scattered light: with application to hydrogen. T. H. HAVELOCK. *Proc. Roy. Soc. (London)* 101A, 154-64(1922).—The object of this paper is to connect the polarization of light scattered by a simple homogeneous medium with the consts. of the dispersion formula for that medium. From 3 consts. in a simple dispersion formula calcn. gives the ratios of the intensities of the two polarized components of scattered light in H for all wave lengths for which the dispersion formula is valid. The numerical results are in substantial agreement with the revized exptl. value 0.0383 obtained by Lord Rayleigh, but one cannot decide between alternative dispersion formulas without more elaborate numerical analysis and further exptl. results. It is shown that certain dispersion formulas which fail to give the correct dispersion in the extreme ultraviolet show a corresponding divergence in the ratios of the intensities of the components of scattered light.

W. F. MEGGERS

The photographic spectrum of the aurora of May 13-15, 1921, and laboratory studies in connection with it. LORD RAYLEIGH. *Proc. Roy. Soc. (London)* 101A, 114-23 (1922).—The spectrum of the aurora photographed on the night of May 14, 1921 with

a prism spectrograph is reproduced. It shows the blue, violet and ultra-violet *negative* bands of N in considerable detail, and the green aurora line 5578 Å. of unknown origin. A number of lab. photographs of the N bands excited in various ways are reproduced for comparison. With at. ray excitation the development of the negative bands can be imitated but other N spectra (line spectrum and second *positive* band spectrum) persistently appear also. The cathode-ray spectrum is free from these extra spectra but the negative bands produced in this way are not developed like those in the aurora, the intensity being much more concd. in the first band of each group. Hard and soft cathode rays behave alike in this respect. These observations are not easily conformable to the view that aurora may be attributed to cathode rays from the sun. The auroral spectrum is also discussed in relation to the upper atmosphere. Assuming that He is the main constituent above 130 kilom. as the theory of diffusion indicates, then it is difficult, on the hypothesis of positive-ray excitation, to explain its absence from the spectrum of this particular aurora which probably reached a height of over 400 kilom. Expts. on artificial mixts. of He and N indicate that the spectrum of He should be visible. With cathode-ray excitation this difficulty is lessened but the different intensity relations among N bands remains. It is possible that the true mode of excitation of the aurora has not yet been suggested.

W. F. MROGERS

**The spectrum of beryllium fluoride.** SNEHAMOY DATTA. *Proc. Roy. Soc. (London)* 101A, 187-94(1922).—The spectrum of  $\text{BeF}_2$ , hitherto unrecorded, is investigated in the region 2200 to 6700 Å. An ordinary C arc is fed with  $\text{BeKF}_2$  and the spectrum recorded with concave grating or quartz spectrographs. Six groups of bands are found, all in the ultraviolet between 2800 and 3400 Å., and all fading off towards the red. The strongest band, at 3009 Å., is studied in detail and is shown to include 3 series of lines. The groups of bands are similar to one of the groups of  $\text{MgF}_2$ , previously described (*C. A.* 15, 3941) and are related to this group in accordance with the formula for alk. earth fluorides,  $\log b \times \log M/a = \text{const.}$ , in which  $a$  and  $b$  are consts. used for the calcn. of series and  $M$  is the mol. no.

W. F. MROGERS

**Optical sensitization.** III. Zinc oxide as an optical sensitizer. CHR. WINTHER. *Z. wiss. Phot.* 21, 141-67(1922).—Certain varieties of  $\text{ZnO}$  act as optical sensitizers on a number of processes. Mixts. of white lead and glycerol turn black in daylight or under the Hg arc only in the presence of  $\text{ZnO}$ , and  $\text{ZnO}$  accelerates the bleaching of eosin and other dyes. The  $\text{ZnO}$  remains completely unchanged. Its activity, which is due to an unknown impurity, is greatest not at its max. of absorption at  $366\mu$ , but at  $280\mu$  where its luminescence is a max.  $\text{ZnO}$  electrodes in aqueous solution develop a p. d. if one is illuminated.  $\text{PbO}$  and  $\text{Pb}_2\text{O}_3$  were also found to act as sensitizers toward cyanine. IV. The formation of ozone by optical sensitization. *Ibid* 168-174.— $\text{O}_2$  was converted into  $\text{O}_3$  in the presence of certain kinds of  $\text{ZnO}$  when exposed through glass to the light from a quartz Hg arc lamp. No change took place in the absence of  $\text{ZnO}$ . When mixts. of  $\text{ZnO}$  were made with other substances, some were without influence and others prevented the reaction. V. *Ibid* 175-185.—On the basis of the results from several photochem. reactions, a theory is developed for the action of sensitizers. The less sensitive a reaction is to light of a certain wave length, the greater is the opportunity for optical sensitization. The sensitizer is converted by the light into another form and the continuous reversal of this process leads to an emission of radiation of shorter wave length which favors the main photochem. reaction.

G. R. FONDA

**The action of light on silver bromide.** E. J. HARTUNG. *J. Chem. Soc.* 121, 682-91 (1922).—By use of the Steele-Grant microbalance (*C. A.* 5, 1541), it was shown that thin films of  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  lose wt. when exposed to sunlight. This is due to loss of halogen and the original wt. is almost completely restored by rehalogenation.

It was found that AgBr decomposes into Ag and Br; and the evidence indicates that the other halides behave similarly. The decompn. is greatly accelerated in a vacuum and in the presence of ozone but oxidizing agents are not essential. H. B. W.

**Fluorescence and photochemistry.** R. W. WOODS. *Phil. Mag.* 43, 737-65 (1922).—A description of expts. in the bleaching of phosphorescent substances mainly with the object of testing the validity of Perrin's theory of fluorescence, according to which fluorescent light is the net result of the explosion of a large no. of mols. of the fluorescent substance in each short interval of time. Usually an intermediate substance is produced by the action of intense light, which is a colored, non-fluorescent compd. having an absorption spectrum quite different from the original fluorescent compd., and which also becomes slowly bleached. In the case of rhodamine in water no colored intermediate is produced. In general the solvent plays an important role. Although Perrin states that fluorescence is independent of the temp., W. has found that the aq. soln. of rhodamine at 100° becomes almost non-fluorescent. To test Perrin's explosion theory, two crucial expts. were carried out, both depending on the suppression of fluorescence, (1) by high temp., (2) by high concn. If bleaching were also suppressed in both cases the support would be regarded as complete, but while it was suppressed in the case of high concn., it proceeded at the high temp. although there was no fluorescence. Another interesting observation is that the rate of decompn. of eosin is not proportional to the light intensity but is disproportionately greater for high intensity. S. C. L.

**Dependence of the velocity of reaction on the concentration in photochemical processes.** M. VOLMER AND K. RIGGERT. *Z. physik. Chem.* 100, 502-11 (1922).—Solns. of anthracene of different concns. were subjected to the radiation (189-200 $\mu$ ) from a quartz lamp, and the ionizing effect was detd. by means of a photoelec. cell. The anthracene solns. were placed between the electrodes of the photoelec. cell. With increase in the concn. of the anthracene, the ionizing effect and the photoelec. current rise rapidly at first, then more slowly and finally reach a const. value. It is shown that in Goldberg's equation,  $v = -dC/dt = kJ_0(1 - e^{-Cd})/d$  (where  $C$  is the concn.,  $e$  the extinction coeff.,  $d$  the density of the radiated layer,  $J_0$  the intensity of the immersing rays and  $k$  a const.), the velocity const.,  $v$ , can be replaced by the strength,  $s$ , of the photoelec. current. Values for  $s$  calcd. by means of the equation  $s = kJ_0(1 - e^{-Cd})/d$  agree closely with exptl. values. H. JERMAIN CREIGHTON

**The chemical action of ionized gases.** G. HOLST AND E. OOSTERHUIS. *Physica* 2, 48-9 (1922).—In a tube contg. Cl with a glow cathode and a cold anode it was observed that the Cl was greatly attracted by the anode and relatively slightly by the cathode. The potential difference between the two electrodes was merely a few volts. It appears that in explaining this one has to consider the following: On passing a current the Cl will be ionized and a number of positive ions formed. Owing to the strong electron affinity of the Cl a no. of negative ions will result. The positive ions move towards the cathode, which is surrounded by a cloud of electrons so that the Cl ions will be neutralized before they reach the wire; they may, as a result of their electron affinity, even take on a negative charge. In the latter case their direction will be reversed and they will move toward the anode. A stronger bombardment against the cathode is not to be expected as a result of the ionization. On the other hand it is impossible for the negative Cl ions to be neutralized at any distance from the anode. They will thus collide with great energy with the metal surface. Indeed, they no sooner come into the vicinity of the electrode, than they are attracted with a force equal to  $e^2/4\pi x^2$ , where  $e$  is the charge of the ion and  $x$  the distance from the electrode. At the instant the ion hits the electrode  $x =$  half the diam. of the ion  $\sigma$ . If now we take  $\sigma = 4.76 \times 10^{-8}$  cm. and  $e = 4.774 \times 10^{-10}$  electrostatic units then the energy of the ions colliding  $= e^2/2\sigma = 2.4 \times 10^{-12}$  ergs, which is as though it came from a source of ion with a temp.



$T = (2.4 \times 10^{-14}) / ((3/2) \times 1.372 \times 10^{-16}) = 11,000^\circ$  in which case it is not surprising that a forcible collision takes place. VINCENT VERMORTEN

Effect of rays from radium, X-rays and ultra-violet rays on glass (CLARK) 19. Photochemistry of the photographic dry plate (WEIGERT) 5. Photosensitiveness of arsenic trisulfide sols (FREUNDLICH, NATHANSOHN) 2.

RUSSELL, A. S.: An Introduction to the Chemistry of Radioactive Substances. London: John Murray. 173 pp. 6s.

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#### 4—ELECTROCHEMISTRY

COLIN G. FINK

Charles L. Norton. ANON. *Elec. World* 79, 1194(1922); 1 illus.—Brief biographical sketch. C. G. F.

Paul J. Kruesi. ANON. *Elec. World* 79, 1244(1922).—Brief biographical sketch. C. G. F.

Electromagnetic motions in electric furnaces. CARL, HERING. *Trans. Am. Electrochem. Soc.* 41, preprint (1922); cf. *C. A.* 15, 1857; *J. Frank. Inst.* 192, 599 (1921).—It is the purpose of the present paper to show how the new law proposed in the former paper may be applied in practice to the production of possible forces for performing desired useful operations, like circulating, stirring, transferring, etc., in elec. furnaces. Guides are given to aid in detg. whether such motions can probably be produced by the current. The former restrictions to only one such motion-producing force were not justified, and many others formerly not accepted are possible.

D. MACRAE

Production of metallic magnesium. S. T. ALLEN. *Chem. Met. Eng.* 26, 987-8 (1922).—See *C. A.* 16, 1707-8. W. H. BOYNTON

History of electric cast-iron melting. W. E. MOORE. *Trans. Am. Electrochem. Soc.* 41, preprint (1922).—Elec.-furnace cast Fe was in the exptl. stage from 1905 to 1914. It was then put into regular operation. Elec. gray cast Fe has been proved a com. success at several plants in the U. S. The elec. process is essentially different from the cupola process in that it reduces rather than increases S; it cuts down Si and Mn losses; it causes no increase in P; superheating produces fluidity with low P; exact control of chem. compn. is possible. The metal produced has physical properties superior to those of cupola metal. The elec. furnace will melt an all-scrap charge costing only a fraction of the cost of a cupola charge. There is an even broader field for the elec. Fe furnace than for the elec. steel furnace. LOUIS JORDAN

Synthetic and electric pig iron sanely considered. ROBERT TURNBULL. *Trans. Am. Electrochem. Soc.* 41, preprint (1922); *Iron Age* 109, 1195.—Low-P pig Fe made in the elec. furnace from scrap-steel turnings is known as synthetic pig Fe. Little if any such Fe is produced to-day on the American continent or in Europe. A number of foundries are now producing gray cast Fe in elec. furnaces from cast-Fe borings. This source of supply will eventually fail and synthetic Fe may again become a part of the industry. Both open-top smelting furnaces and steel furnaces have been used for the production of synthetic Fe. No advances in the production of pig Fe from ore in the elec. furnace have been made in recent years. Both shaft and open-top furnaces of considerable size are operating in Sweden but are far from economical. The shaft

furnace has presented no advantages over the open-top furnace and has considerable disadvantages.

LOUIS JORDAN

**Cast iron as produced in the electric furnace and some of its problems.** G. K. ELLIOTT. *Trans. Am. Electrochem. Soc.* 41, preprint (1922); *Iron Age* 109, 1225-6.—The history of the development of the elec. furnace for the prepn. of cast Fe is outlined. The refining on a basic bottom of cupola-melted metal is the field of widest possibilities for the elec. furnace for cast Fe. Ability to refine in addition to melting and increased power to superheat are 2 desirable characteristics lacking in the cupola but outstanding in the elec. furnace. Elimination of S is the most striking reaction in the basic elec. furnace. Anomalous results have been reported as to the effects of S on irons. Low S may be simply an indication that the iron has passed through a strong refining treatment and better quality in such a case may be due to elimination of little known impurities, as O or N. One of the moot questions of cast Fe is whether or not Fe oxide can exist in molten cast Fe in the presence of the usual amt. of C, Si, and Mn and, if it is present, whether its influence is harmful or beneficial. The question of O in cast Fe, as well as that of N and other gaseous elements, must remain unsettled until satisfactory analytical methods are available. The superheating possible in the elec. furnace is of advantage in producing fluidity with any compn. of Fe. There is evidence that elimination of CO and CO<sub>2</sub> in cast Fe has a retarding effect on the pptn. of graphite. This factor may contribute to the increased strength and soundness of elec.-furnace cast Fe.

LOUIS JORDAN

**Hydrogen overvoltage and current density in the electrodeposition of zinc.** U. C. TAYNTON. *Trans. Am. Electrochem. Soc.* 41, preprint (1922).—A study of elec. conditions necessary for a good deposit of Zn from electrolyte used in commercial practice which is necessarily impure. The main requisites are a high c. d., (100 amp. per sq. ft.) and a smooth deposit. Expt. shows that a high c. d. increases the H<sub>2</sub> overvoltage for metals, (Pb, Cu, Fe, Ni, Co, Sb, impurities in electrolyte), above the value 0.75 v. which is the potential of Zn on the hydrogen scale. This prevents the evolution of H<sub>2</sub> on the cathode with the usual bad results. A smooth deposit is best maintained (a) by high electrolytic cond., best given by high acid concn., (250-300 g. free H<sub>2</sub>SO<sub>4</sub> per l.); this permits low cell voltage, (3.5 volts), and restrains "trees," which lower current density; (b) by adding a colloid, such as glue or gelatin, which diminishes interfacial tension at the contact surface of the cathode and electrolyte; this gives a small contact angle, preventing H bubbles from adhering to the cathode; a colloid also restrains the crystalline growth of the cathode; (c) by a rapid upward movement of electrolyte past the cathode surface; this is usually automatic if high c. d.'s are used. C. H. E.

**Effect of impurities on electrolytic zinc.** G. D. SCHOLL. *Chem. Met. Eng.* 26, 595-602(1922).—An account of studies made (1918) at the Keokuk Iowa plant of the River Smelting and Refining Co. Severe corrosion commenced several hrs. after an addition of impurity. The electrolyte was pure ZnSO<sub>4</sub> 70-80 g. per l. and 0-6 g. free H<sub>2</sub>SO<sub>4</sub> per liter. A first-class Zn deposit is hard, smooth and densely cryst. and shows a current efficiency of 90% or above. Cu was added up to 1 part per 100,000 with 92% current efficiency and indications are that Cu may without danger go as high as 5 parts per 100,000. Co is extremely dangerous in concns. over 1 part per million, and gives excessive corrosion with a blunt and fibrous structure. Sb in excess of 1 part in 5 million is decidedly objectionable. Corrosion is excessive, and effects are striking and distinctive. Sb gives a "carrot-like bamboo" structure after 23-30 hrs., and a "cauliflower-mushroom" structure after 48 hrs. Arsenic causes serious loss of current efficiency in concn. as low as 1 part per 100,000. Deposits are marked by a shattering of the characteristic structure given by Sb. Ni gives a surface similar to that given by Co. Excessive Ni gives concentric banded borders surrounding corrosion areas, and

in concn. of 1 part per 100,000 gives current efficiency of 85%. Of all impurities the effect of Ni is most markedly affected by the presence of other impurities.

C. H. ELDRIDGE

**Throwing power and current efficiency of zinc-plating solutions.** W. G. HORSCH AND TYLER FUWA. *Trans. Am. Electrochem. Soc.* 41, preprint (1922).—Throwing power is described as the ability of an electrolyte to give a uniform deposit even on objects of irregular contour. With the assumption that high throwing power is caused by having in soln. a relatively large number of conducting ions and a small number of ions of the metal to be plated out, several of well known solns. were tried out. Plating baths of which the principal constituents were sulfates, fluoroborates or zincates showed low throwing power. Alkaline cyanide baths, having the compn. NaCN 53.2 g., Zn cyanide 59.2, NaOH, 43.8,  $\text{Na}_2\text{CO}_3$ , 9.5 g.,  $\text{Al}_2(\text{SO}_4)_3$  4.7, "lignol" 11.8 g. per 1000 cc.  $\text{H}_2\text{O}$  gave best results. Such a bath showed high throwing power, 80% efficiency, low voltage. Best operating conditions were: 40°, moderate stirring, 2 amp. per dm.<sup>2</sup>, with a composite anode of Zn and duriron, the latter forming 30% of the total anode surface. "Lignol" was the best addition agent.

C. H. ELDRIDGE

**Conductivity of copper-refining electrolytes.** E. F. KERN AND M. Y. CHANG. *Trans. Am. Electrochem. Soc.* 41, preprint (1922).—The sp. conds. of solns. of  $\text{H}_2\text{SO}_4$ ,  $\text{CuSO}_4$ , and mixts. of the two were detd. at 25°, 40°, and 55°. Concn. were 0.5–2 g. per l. Tables and curves show the effect of varying conditions. The Cu content of the refining electrolyte should be kept between 30 and 35 g. per l., and free  $\text{H}_2\text{SO}_4$  as high as economy permits up to 175 g. per l. With higher free acid the soly. of  $\text{CuSO}_4$  decreases rapidly, and also, the added increase in cond. with more concd. acid is relatively not so rapid. Maintain the temp. as high as economy permits. The economical limit seems to be 55°. Keep the Ni and Fe content as low as possible, as both Fe and Ni sulfates depress the cond. of the electrolyte. Arsenic in soln. but slightly decreases cond.

C. H. ELDRIDGE

**Electrodeposition in automotive repair work.** B. H. THOMAS. *Automotive Industries* 43, 418–20(1920).—During the war a new process was developed in the British army repair shops whereby worn-down parts such as stub axles, wheel hubs, shaft ends, etc. were built up quickly and efficiently and subsequently showed good wearing qualities. A layer of Fe approx. 2 mm. thick was deposited on any cylindrical surface of wrought Fe or mild or cast steel. It could not be chipped away with a chisel, and was so closely blended to the base metal that photomicrographs did not reveal the boundary. It was deposited without preliminary coppering and was subjected to red heat without injury. A satisfactory deposit could not be obtained on Al or cast Fe. The cleansing process consists of 7 stages and on it success depends: (1) removal of all grease by gasoline; (2) heating 12 hrs. at 90° in a bath contg. 5% NaOH + 5%  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ; (3) removal by  $\text{H}_2\text{O}$  of the soln., scouring and waxing of areas not be treated; (4) covering until the moment of treating under (5) with a protective coat of equal parts of tallow and linseed oil; (5) removal of this and immersion in a bath like (2) only at 20° and with the parts as cathode and a sheet Fe anode with passage of current and evolution of  $\text{H}_2$  for 3 min.; (6) immersion for a few sec. in a bath of 50%  $\text{HNO}_3$  to create enough corrosion for max. adhesion; (7) removal of all soln. and immersion in a bath of 25%  $\text{H}_2\text{SO}_4$ , with the parts as anode and with passage of current to evolve  $\text{O}_2$  and then  $\text{H}_2$  with 3-min. reversals until the surface is a fine white mat. Then plating with Fe in soln. of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4$  (75 g. of the crystd. salt per l.), with a c. d. of 0.33 amp. per dm.<sup>2</sup>. The rate of deposition was 0.005 mm. thickness per hr. in 30-l. vats. Either beeswax 90, rosin 10 or bitumen 70, paraffin wax 30 is recommended for waxing. A complete tabulation is given of the necessary plant equipment, with precautions and causes of failure. With a const. current, the rate of deposition can be calcd. beforehand within 2.5%.

C. C. DAVIS

**Electrolytic deposition of iron for building up worn or undersized parts.** DAVID R. KESLOGG. *Trans. Am. Inst. Mining and Met. Eng.*, preprint No. 1137-S(1922).—A procedure similar to that used in the Brit. Army repair shops and described in the preceding abstract, was used to deposit smooth, tough, adherent coats of Fe upon worn or undersized motor shafts, plug and thread gages, press fits, etc. The piece to be plated was first cleaned with gasoline and then made the cathode in an alk. bath of 5% NaOH and 5%  $\text{Na}_2\text{CO}_3$ , with a current of 0.5 to 0.8 amp. per  $\text{cm}^2$ . After a 3-min. treatment in this bath the piece was rinsed in tap water and then made the anode in a 20% to 30% soln. of  $\text{H}_2\text{SO}_4$  for the same period. The plating soln. contained 75 g. of crystd.  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  per l. and the plating current was 0.33 amp. per  $\text{dm}^2$ , with an efficiency of 75%. The coating wore practically as well as the original motor shaft material and its Brinell hardness was 220. Small amts. of  $\text{FeCO}_3$ , "mud" and powdered charcoal were added to prevent oxidation in the plating soln., which was stirred continuously. Coatings made from a hot, concd. soln. such as was used by Macfadyen (*C. A.* 15, 25) and current densities up to 10 amp. per  $\text{dm}^2$  were softer and more easily machined than those from the cold, dil. soln.; also the efficiency of deposition increased to nearly 100%. Cast Fe, though it emerged from the cleaning process with a slimy coating of graphite, took on a coating that was entirely satisfactory. The plating soln. was contained in a stoneware jar; any wood in contact with the soln. caused the deposits to be hard, brittle, specular, and non-adherent. Com. grades of chemicals proved satisfactory.

C. C. VAN VOORHIS

**Electrolytic generation of hydrogen and oxygen with special reference to the utilization of off-peak power.** WM. G. ALLAN. *Trans. Am. Electrochem. Soc.* 41, preprint (1922).—The economics of the problem are set forth in such a form that the costs of the gases under widely varying conditions as to the cost of elec. energy, rates of depreciation, and current density can be ascertained by reference to a series of curves. A new type of cell is described. It requires for the generation of each cu. ft. of H per hr. only 3.37 sq. in. of floor space and 2.81 lbs. of electrolyte. It is adapted to operate under widely varying conditions of c. d. of projected electrode area, without too great a sacrifice of energy efficiency. It is thus adapted to different rates of gas production, according to the cost of power at any particular time of a 24-hr. day. The higher the rate of gas production, the less the influence of the fixed charges in the total cost of the gases, while depreciation does not increase at a rate which is proportionate to the rate of gas production. As a result, at high c. d.'s the cost of power becomes the major item in the total cost of the gases, and with cheap off-peak power, many processes which up to the present have been excluded from consideration, now come at least within the range of possibility and others are definitely placed in the class of commercially feasible processes. Present and future possible uses of O and H are given.

D. MACRAE

**A study of the effect of impurities on storage batteries.** HELEN C. GILLETTE. *Trans. Am. Electrochem. Soc.* 41, preprint (1922); *Chem. Met. Eng.* 26, 981-3(1922).—A test was made of the effect of the 12 common metals and of HCl,  $\text{HNO}_3$  and acetic acid on lead (Prestolite) storage batteries. Contrary to general expectations, most impurities were harmless. Mn and Pt were the only ones to produce a lasting bad effect on the amp.-hr. capacity and voltage characteristic. These same metals caused rapid loss of charge on standing, and a marked shortening of life. Cd and Ag also were detrimental to life and caused rapid loss of charge.

C. H. ELDRIDGE

**Measurement of pressures in vacuum type lamps.** DUNCAN MACRAE. *Trans. Am. Electrochem. Soc.* 41, preprint (1922).—The tip of the lamp is removed in an evacuated glass system by means of an Fe plunger electromagnetically operated. The resulting pressure is measured with a McLeod gage. Well exhausted factory product lamps show 4-10 bars before "flashing," less than 1 bar after flashing, and after 1000

substances, chrome alum and KBr suggesting themselves. There is no increase in fog, such as follows the use of  $\text{NH}_4\text{OH}$ . Films are best sensitized in a bath of water, alc.,  $\text{NH}_4\text{OH}$ , and stock dye soln. Pinacyanol gives good results in dil. alc. soln. with  $\text{NH}_4\text{OH}$ , but carefully washed plates bathed in water and dye soln. keep better and are almost as sensitive. Dicyanin gives greater sensitiveness and goes further into the infrared when used with  $\text{NH}_4\text{OH}$  than with water alone. Certain brands of orthochromatic plates surpass erythrosin-bathed plates, but no stock panchromatic plate equals pinacyanol-bathed plates. Many spectrograms are given, for which the original paper must be consulted.

L. DERR

Preparing light-sensitive photographic papers. CHAS. E. MULLIN. *Photo-Era* 43, 30-5, 92-3, 138-41, 204-6(1922).—A compilation of formulas. CHAS. E. MULLIN

Toning of photographic silver images. A. R. RIDDLER. *Trans. Proc. Roy. Soc. S. Australia* 44, 293-9(1920).—In sulfide or Cu toning, though the purple and purple-black tones may be good, the lighter tones may show troublesome color differences. The difficulty appears traceable to incomplete elimination of  $\text{AgNaS}_2\text{O}_4$  even by prolonged washing. It is convertible into a sol. tetrathionate by 5 min. immersion in  $\text{K}_2\text{C}_2\text{O}_8$  (0.6% soln.), followed by 30 min. washing. Rich and uniform tones are obtained.

L. DERR

The action of light on silver bromide (HARTUNG) 3. Isocyanines and carbocyanines as photographic sensitizers (POPE) 10.

Nitrocellulose sheets or films adapted for photographic purposes. P. C. SEHL. U. S. 1,415,059, May 9. An antistatic transparent film is formed of nitrocellulose together with acetone, MeOH, fusel oil, camphor, glucose, glycerol and  $\text{H}_2\text{O}$ . Cf. C. A. 15, 3255.

## 6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

Chromic thiocyanates. I. Preparation, composition, and properties. NIELS BJERRUM. *Z. anorg. allgem. Chem.* 118, 131-64(1921); cf. C. A. 1, 2211, 2771; 15, 1466.—It has been known that  $\text{Cr}^{+++}$  and  $\text{CNS}^-$  in concd. soln. form  $\text{Cr}(\text{CNS})_6^{---}$  and that in dil. soln. and light the reverse action takes place. From Werner's hypothesis the formation of the complex ion could be expected to take place by successive replacement of  $\text{H}_2\text{O}$  in hexa-aquo chromic ion by from 1 to 6  $\text{CNS}^-$ . In the description of the phenomena attending these changes, B. seeks to replace the usual qual. indefinite statements by somewhat more definite quant. results in the language of physical chemistry. In concd. solns. at room temp. the rate of formation of the complex ions is rapid but at concns. below 1 M is very slow. For a soln. of  $\text{Cr}(\text{NO}_3)_3$  0.01 M and  $\text{NH}_4\text{CNS}$  0.06 M at 25°, measurements of elec. cond. at definite time intervals showed the following ratios of  $\text{CNS}$  to Cr in the complex: 1 hr., inappreciable; 4 days, 0.46; 8 days, 0.85; 13 days, 1.20; 48 days, 1.43. For solns. 0.01 M in  $\text{Cr}(\text{NO}_3)_3$  and having ratios of  $\text{KCNS}$  to  $\text{Cr}(\text{NO}_3)_3$  varying from 1 to 20 the following ratios of  $\text{CNS}$  to Cr in the complex at equil. at 50° are found: 1, 0.58; 2, 0.93; 3, 1.15; 4, 1.29; 6, 1.58; 10, 1.95; 20, 2.40. For a soln. of  $\text{Cr}(\text{CNS})_3$  0.05 M and  $\text{KCNS}$  0.5 M the ratio is 3.13; 0.5 M  $\text{K}_2\text{Cr}(\text{CNS})_6$ , 4.07; and  $\text{K}_2\text{Cr}(\text{CNS})_6$  0.5 M and  $\text{KCNS}$  1.5 M 5.03. At 50° equil. is attained in 2 days, at 100° in 15-30 mins. but at ordinary temps. years are required for solns. below 0.01 M to attain equil.  $\text{Cr}(\text{H}_2\text{O})_4(\text{CNS})^{++}$  and  $\text{Cr}(\text{H}_2\text{O})_4(\text{CNS})_2^+$  compds. cannot be extd. from aq. soln. with  $\text{Et}_2\text{O}$  and in this respect are different from other thiocyanate chromic salts. They have not been prepd. in the form of

solid compds. but give a red-violet soln. If  $\text{Cr}(\text{CNS})$ ,  $\text{Cr}$ , and  $\text{CNS}$  are the molal concns. of the monothiocyanate complex, the thiocyanate free Cr, and the ionizable CNS, resp., and  $t$  is the time in minutes,  $d(\text{CrCNS})/dt = k(\text{Cr})(\text{CNS})$ . At  $25^\circ$ ,  $k = 0.0018$ , at  $50^\circ$ , 0.13, and since the equil. const. at  $50^\circ$  is 328, the *decompn. velocity const.* of  $\text{Cr}(\text{H}_2\text{O})_5(\text{CNS})^{++}$  is 0.00040.  $\text{Cr}(\text{H}_2\text{O})_5(\text{CNS})_2$  is easily sepd. from other thiocyanate chromic compds. extd. by  $\text{Et}_2\text{O}$  because its distribution coeff. is independent of the acidity of the aq. soln. while the others are extd. by  $\text{Et}_2\text{O}$  only when the aq. soln. is acid. The *mol. cond.* of  $\text{Cr}(\text{H}_2\text{O})_5(\text{CNS})_2$  at  $14^\circ$  is 1.36 in 0.047  $M$  soln. It probably dissociates as follows:  $\text{Cr}(\text{H}_2\text{O})_5(\text{CNS})_2 = \text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_2\text{OH}^- + \text{H}^+$ . Approx. analyses of the solid confirm the presence of 3  $\text{H}_2\text{O}$ . The *distribution coeff.* of  $\text{Cr}(\text{H}_2\text{O})_5(\text{CNS})_2$  between  $\text{H}_2\text{O}$  and  $\text{Et}_2\text{O}$  varies with the age and method of prepn. of the sample. This indicates that it exists in 2 isomeric forms in accord with Werner's theory.  $\text{Cr}(\text{CNS})_3$  and  $\text{Et}_2\text{O}$  form  $\text{Cr}(\text{CNS})_2(\text{Et}_2\text{O})_2$  with the evolution of much heat. This compd. is decomposed by  $\text{H}_2\text{O}$  liberating the  $\text{Et}_2\text{O}$ . The *molar extinction coeffs.* of  $\text{Cr}(\text{CNS})_6^{---}$  (*i. e.*,  $K_2\text{Cr}(\text{CNS})_6$ ) were detd. by the same method as used by B. for  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$  and are given for 10 wave lengths between 730 and 440 micromillimeters as follows: 730  $\pm$  30, 1.38; 666  $\pm$  19, 9.2; 626  $\pm$  15, 51.3; 591  $\pm$  12, 121.2; 564  $\pm$  11, 149.2; 539  $\pm$  9, 119.4; 519  $\pm$  8, 78.8; 486  $\pm$  6, 33.6; 462  $\pm$  8, 48.9; 440  $\pm$  14, 95.8. While salts of  $\text{Cr}(\text{CNS})_6^{---}$  can be preserved indefinitely in the solid state, in alk., acid, or neutral soln. they decompose. In the dark 0.12  $\text{CNS}^-$  per Cr is formed in 5 hrs. in 0.1  $M$  to 0.001  $M$ . In 0.01  $M$  NaOH 8 times as much is formed in the same time. In 0.001  $M$  soln. 10 times as much is decomposed in diffused daylight as in the dark. For  $\text{Cr}(\text{CNS})_6^{---} = \text{Cr}(\text{CNS})_3^- + \text{CNS}^-$  the velocity const.  $k = \log(1-a)/0.4343 t$ , in which  $a$  is the no. of  $\text{CNS}^-$  per Cr atom and  $t$  the time in mins., is 0.0050 for 0.1 and 0.001  $M$  solns. in  $\text{H}_2\text{O}$ ; 0.00041 for 0.001  $M$  in 0.1  $N$  HCl; 0.00060 for 0.001  $M$  in 0.01  $N$  NaOH—all in the dark. In diffused daylight  $k = 0.0017$  for 0.01  $M$  solns. in alc. or  $\text{H}_2\text{O}$  and 0.0064 for 0.001  $M$  in 0.1  $N$  HCl. In contrast to all other thiocyanate chromic ions, the *velocities of decompn.* of  $\text{Cr}(\text{CNS})_6^{---}$  are independent of the acidity or alky. of the soln. Its decompn. in  $\text{Et}_2\text{O}$  is very rapid and is characterized by the formation of 3 layers. The lowest is an aq. soln., the top one a dil. ethereal soln., and the middle one a small strongly colored layer which consists of a concd. soln. of  $\text{H}_2\text{Cr}(\text{CNS})_6$ . By working rapidly it is possible to confirm the relation  $a/b(\text{H}^+)^3 = K$  to the extent that the addition of HCl to the water layer has an enormous influence on the distribution ratio  $a/b$ . *Pyridine* and *quinoline* salts are well suited to the detection and identification of  $\text{Cr}(\text{CNS})_6^{---}$ .  $(\text{C}_5\text{H}_5\text{N})_3\text{Cr}(\text{CNS})_6 \cdot \text{H}_2\text{O}$  has a soly. product of  $2-5 \times 10^{-7}$  and  $(\text{C}_9\text{H}_7\text{N})_3\text{Cr}(\text{CNS})_6 \cdot \text{H}_2\text{O}$  one of  $8-34 \times 10^{-13}$  and its formation on the addition of quinoline sulfate is a very delicate test for  $\text{Cr}(\text{CNS})_6^{---}$ . II. *Preparation, composition, and properties.* *Ibid* 119, 39-51 (1921).— $\text{Cr}(\text{H}_2\text{O})(\text{CNS})_5^{--}$  is obtained in a solid compd. by pptn. with quinoline sulfate to form  $(\text{C}_9\text{H}_7\text{N})_2\text{Cr}(\text{CNS})_5 \cdot 2\text{H}_2\text{O}$ . This salt loses one  $\text{H}_2\text{O}$  on drying over  $\text{CaCl}_2$ . Its soly. product in  $\text{H}_2\text{O}$  is about  $2 \times 10^{-9}$ . It is more sol. in alc. A soln. contg. the ion was prepd. from the quinoline salt. Colorimetric tests on this soln. showed that not more than 0.0012 of the CNS was ionized. Qual. expts. show that the distribution coeff.  $K$  is about 4, when  $K = a/b(\text{H}^+)^3$  in which  $a$  is the molar concn. in  $\text{Et}_2\text{O}$  and  $b$  that in  $\text{H}_2\text{O}$ . An aq. soln. of  $\text{Cr}(\text{H}_2\text{O})(\text{CNS})_5^{--}$  is red-violet; its color recalls that of  $\text{Cr}(\text{CNS})_6^{---}$ . In  $\text{Et}_2\text{O}$  the free acid has a more greenish violet color. It quickly turns to green as a result of change to  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_4$ . Velocity constants for this change at  $16-18^\circ$  were found to be as follows at various concns. of  $\text{H}^+$ : 0.00014 at  $0.73 \times 10^{-3}$ ; 0.0003 at  $0.18 \times 10^{-4}$ ; 0.018 at about  $10^{-6}$  in the dark; 0.002 at about  $10^{-1}$  in diffused daylight; and 0.005 in  $\text{Et}_2\text{O}$  in the dark.  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_4^-$  has not been obtained in a well defined solid compd. but solns. have been obtained which contained their Cr and CNS in such a tetrathiocyanate compd.

These solns. result from a system of  $\text{Et}_2\text{O}$  extns. of a soln. of the dry residue from the evapn. of a soln. of  $\text{Cr}(\text{H}_2\text{O})_4(\text{CNS})_2$ . The sepn. of the tetrathiocyanate by this method depends on the fact that  $\text{Et}_2\text{O}$  without the addition of acid removes chiefly  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_2$  and after acid addition removes both  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_4^-$  and  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_2$ . In contrast to  $\text{H}_2\text{Cr}(\text{CNS})_6$  and  $\text{H}_2\text{Cr}(\text{H}_2\text{O})(\text{CNS})_5$ ,  $\text{HCr}(\text{H}_2\text{O})_2(\text{CNS})_4$  is fairly stable in  $\text{Et}_2\text{O}$  soln. It decomposes at a rate of less than 0.05 per day. In neutral aq. soln. 0.30 decomposes per day; while in acid soln. only 0.05 to 0.08 is decomposed. Its distribution coeff.  $K = a/b\alpha(\text{H}^+)$ , in which  $\alpha$  is the degree of dissociation of  $\text{HCr}(\text{H}_2\text{O})(\text{CNS})_4$ , has been found to be 9.4. An oily quinoline compd. ppts. when 1 *N* quinoline sulfate is added in excess to a concd. acid soln. contg.  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_4^-$ . On the other hand quinine chloride and strychnine nitrate ppt. even very dil. acid solns. The ppt. is nearly white with bluish tint and flocculent but appears slightly crystalline under the microscope. It varies in compn. and its nature is not at present clearly understood. According to Werner's theory of the position of the 6 groups in the complex, a *cis* and *trans* form of  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_4^-$  should exist. There are slight indications that forms with different distribution coeffs. do exist. **III. Methods of analysis.** *Ibid* 51-68.—Cr was always detd. by titration with thiosulfate after oxidation to chromate with  $\text{H}_2\text{O}_2$  in alkaline soln., boiling off the  $\text{H}_2\text{O}_2$  and the addition of  $\text{HCl}$  and  $\text{KI}$ . If the substance to be analyzed contained CNS, this was first oxidized by  $\text{HNO}_3$  on the water bath. Titration with  $\text{AgNO}_3$  gives the total number of equivs. of  $\text{CNS}^-$ ,  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_4^-$ ,  $\text{Cr}(\text{H}_2\text{O})(\text{CNS})_5^-$ , and  $\text{Cr}(\text{CNS})_6^{3-}$ . If after this titration the remaining complexes are decomposed with  $\text{NaOH}$ , the soln. cooled and acidified, the remainder of the  $\text{CNS}^-$  may be titrated. If CNS and Cr are to be detd. in the same sample, the Cr is pptd. with  $\text{NH}_4\text{OH}$  and sepd. from the soln. by filtration. Ionizable CNS was detd. colorimetrically after the addition of  $\text{Fe}(\text{NO}_3)_3$ . The procedure for the detn. of the quantities of the different CNS complexes in mixts. is as follows: First, the  $\text{Cr}(\text{H}_2\text{O})(\text{CNS})_5^-$  and  $\text{Cr}(\text{CNS})_6^{3-}$  are pptd. as quinoline salts and their relative amts. detd. from analysis of the ppt. for Cr and CNS; then, of the unpptd. complexes,  $\text{Cr}(\text{H}_2\text{O})_2(\text{CNS})_2$  is extd. with  $\text{Et}_2\text{O}$  from neutral soln. and  $\text{Cr}(\text{H}_2\text{O})(\text{CNS})_4^-$  from acid soln. From the soln. in which  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Cr}(\text{H}_2\text{O})_5(\text{CNS})^{2+}$ , and  $\text{Cr}(\text{H}_2\text{O})_4(\text{CNS})_2^+$  remain unextd. the  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  is pptd. as chrome alum by the addn. of  $\text{K}_2\text{SO}_4$  and alcohol and the relative amounts of the remaining compds. are detd. from analysis of the soln. for Cr and CNS. The quinoline pptn., the ether extn. and the alum pptn. are described in detail. No method for the detn. of basic complexes which seem to be present in the solns. has yet been worked out. **IV. Chemical equilibrium between the thiocyanate chromic complexes.** *Ibid* 179-201.—From the elec. cond. of solns. of 0.01 *M*  $\text{Cr}(\text{NO}_3)_3 + \text{KCNS}$ , 0.01 *M*  $\text{Cr}(\text{NO}_3)_3 + 2\text{KCNS}$ , and 0.01 *M*  $\text{Cr}(\text{NO}_3)_3 + 3\text{KCNS}$  at 50° the ratio of CNS to Cr in the complex was found to be 0.64, 0.94, and 1.19, resp. Chem. analysis gave the following comparable results: 0.58, 0.93, and 1.15. These and other analyses at varying concns. give the following av. values of the *equil. consts.*  $K_{\text{Cr}(\text{CNS})_n} = [\text{Cr}(\text{CNS})_n]/[\text{Cr}(\text{CNS})_{n-1}][\text{CNS}]$ : 328, 17.5, 4.56, 1.93, 0.81, and 0.41 when  $n = 1, 2, 3, 4, 5$ , and 6, resp. With the aid of the relation  $A = RT \ln K$ , the following values of *A* corresponding to the above *equil. consts.* are obtained: 3710, 1840, 970, 420, -130, and -570 cal. These values show that the *affinity* (or *free energy* of) formation of different thiocyanate complexes decreases strongly with the number of thiocyanate groups already in the complex. With the aid of the *equil. consts.* obtained a series of curves is plotted from which the approx. mol. per cents of the various complex ions may be read for any known concn. of ionogen thiocyanate. Expts. at 100° and 25° show that the complex formation between Cr and CNS does not change rapidly with the temp.

D. MACRAE

A simple method for the preparation of crystalline gypsum. L. BOURGOIS. *Bull.*

*soc. chim.* 31, 160-1(1922).—Small transparent crystals of gypsum were observed in a beaker contg. pieces of plaster in contact with  $\text{HNO}_3$ , which had been standing several months at ordinary room temp. After several expts. the following method of prep. cryst. gypsum was adopted: Mix 3 vols. of  $\text{HNO}_3$  (40° Bé.) with 1 vol. of water, heat nearly to boiling and sat. with  $\text{CaSO}_4$ . Decant the mother liquor or filter through glass wool. Gypsum crystals will begin to form slowly at the end of 8 days and continue for over a week. The crystals attain lengths of 15 mm. and widths of a few mm. They are characterized by their clearness and are not fibrous in appearance as crystals formed in solns. with  $\text{HCl}$ ,  $\text{NaCl}$ , or  $\text{Na}_2\text{S}_2\text{O}_4$ . The best crystals were obtained in a  $\text{HNO}_3$  soln. after it had stood 3 months at room temp. A. R. ALBOUZE

**Purification of phosphoric oxide.** G. I. FINCH AND R. H. K. PETO. *J. Chem. Soc.* 121, 692-3(1922).—The purest samples of commercial  $\text{P}_2\text{O}_5$  obtainable usually contain impurities such as the lower oxides of P, which can be detected by their reducing action on solns. of  $\text{AgNO}_3$  or  $\text{HgCl}_2$ . These in general are powerful catalyst poisons. Purification can be effected by subliming the mixt. at bright red heat in a current of dry O with an app. consisting of an inverted T-tube of iron pipe the middle part of which is heated in a furnace. At one end of the horizontal tube dry O is admitted; from the other end, to which is cemented a piece of combustion tubing, the sublimed  $\text{P}_2\text{O}_5$  is discharged into a large bottle. From a trap at the end of the vertical piece the crude material is fed as required. In 1 hour 50 g. of pure  $\text{P}_2\text{O}_5$  were prepd. H. L. OLIN

EPHRAIM, FRITZ: *Anorganische Chemie*. Dresden and Leipzig: Th. Steinkopff, M 180.

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

**New methods employed for determining the reaction of solutions.** RENÉ FABRE. *J. pharm. chim.* 25, 26-33, 58-63(1922).—A review of the electrometric and colorimetric methods of measuring  $\text{H}^+$  concns. S. WALDBOTT

**The use of the iodine electrode in potentiometric titrations.** I. M. KOLTHOFF. *Rec. trav. chim.* 41, 172-91(1922); cf. *C. A.* 15, 996.—The theory of the  $\text{I}_2$  electrode is explained and the results obtained by Lottermoser and Steude (*C. A.* 16, 671) are confirmed. Procedures are outlined for the titration of  $\text{I}^-$  with  $\text{Ag}^+$  and with  $\text{Hg}(\text{ClO}_4)_2$ , for the analysis of  $\text{HgCl}_2$  and of  $\text{Ti}^+$  compds. E. J. WITZEMANN

**A simple method of electrometric titration in acidimetry and alkalimetry.** P. F. SHARP AND F. H. MACDOUGALL. *J. Am. Chem. Soc.* 44, 1193-6(1922).—With electrodes of Pb amalgam and Cd amalgam, a series of half cells has been prepd. which are electromotively equiv. to H electrodes in contact with solns. in which the  $\text{H}^+$  concns. are, resp.,  $10^{-4}$ ,  $10^{-4.7}$ ,  $10^{-5}$ ,  $10^{-6}$ ,  $10^{-7}$ ,  $10^{-8}$ ,  $10^{-9}$  and  $10^{-10}$ . The cells are formed by using 12-12.5% Pb or Cd amalgams and varying quantities of KI in the case of Pb-Hg cells and of KI and  $\text{CdSO}_4$  in the case of Cd-Hg cells. W. T. H.

**Modifications of the Pregl method of micro-analysis.** FRIEDRICH HOLTZ. *Ber.* 55B, 1496-7(1922).—Instead of using a bomb furnace for the detn. of halogen and S by the Carius method it is recommended to heat the miniature Carius tube in a bath of methylidiphenylamine. Place 50 g. of the amine in a wide-mouthed flask about 10 cm. in diam. and 15 cm. tall. Stopper the flask with a fresh cork stopper carrying an air condenser and some brass tubing which extends to near the bottom of the flask. For the Carius tubes, use soft-glass tubing about 17 cm. long and 10 mm. outside diameter. After filling the Carius tube with 0.5 cc.  $\text{HNO}_3$ , 3-5 mg. of substance and a crystal of  $\text{AgNO}_3$  or  $\text{BaCl}_2$ , place it in the brass tubing with the aid of a wire and stopper



the tubing. In the S analysis, a little  $\text{Br}_2$  helps to shorten the digestion period, which is usually 8 hrs. Heat the amine by means of a flame beneath the flask. In the detn. of N by the Dumas method the incomplete decompn. of N oxides can be prevented by filling the tube as follows: asbestos plug, 7 cm. of CuO in wire form, 11 cm. of reduced Cu wire, asbestos plug, then for each analysis a fresh 7 cm. of CuO in wire form, 4 cm. of CuO powder mixed with the substance and a little  $\text{KClO}_3$ , and 5 cm. of CuO wire. The furnace recommended by Pregl is also modified somewhat to make sure the contents of the tube are properly heated. For drying substances, a slight modification of the Pregl drying oven is proposed. W. T. H.

**Volumetric methods for the determination of dithionic acid.** A. FISCHER AND W. CLASSEN. *Z. angew. Chem.* 35, 198-8(1922).—Salts of  $\text{H}_2\text{S}_2\text{O}_6$  are stable toward cold, dil. mineral acids and toward oxidizing agents. If boiled with HCl, however, they are decomposed into sulfate and sulfurous acid. The latter may be distd. off and absorbed in a known vol. of standard  $\text{I}_2$  soln. and the excess of the latter detd. by titration with  $\text{Na}_2\text{S}_2\text{O}_3$ . A dil. acid  $\text{KMnO}_4$  soln. was found to be a better absorbent than  $\text{K}_2\text{Cr}_2\text{O}_7$  soln. and  $\text{I}_2$  better than  $\text{KMnO}_4$ . The decompn. of the dithionate should take place in an atm. of  $\text{CO}_2$  and the absorbent should be kept cold with ice water. Most other acids of S are decomposed more readily than  $\text{H}_2\text{S}_2\text{O}_6$  so that it is not difficult to est. dithionate in the presence of other closely related acids. W. T. H.

**A test for thiosulfate or nitrite ions.** P. FALCIOLA. *Gazz. chim. ital.* 52, I, 179-82 (1922).—If a soln. contg.  $\text{S}_2\text{O}_3^{--}$  and  $\text{NO}_2^-$  is made faintly acid by the addition of mineral acid, org. acid or even alum, enough  $\text{HNO}_3$  and  $\text{H}_2\text{S}_2\text{O}_6$  are liberated to enter into reaction. A yellow, green or brown color is produced depending upon the concn. The test may be used for either  $\text{S}_2\text{O}_3^{--}$  or  $\text{NO}_2^-$  ions. At the end of the paper there is a discussion on the various colorimetric tests that have been proposed hitherto for the identification of various S compds. E. J. WITZEMANN

**The colorimetric determination of arsenic by means of quinine molybdate.** D. CHOUGHAK. *Ann. chim. anal. chim. appl.* [2] 4, 138-42(1922).—A: Dissolve 3.5 g.  $\text{Na}_2\text{CO}_3$  in 50 cc. of water in a 100-cc. volumetric flask, add 9.5 g.  $\text{MoO}_3$ , heat on the water bath till soln. is complete, let cool, and make up to 100 cc. B: Dil. 25 cc.  $\text{HNO}_3$  (d. 1.34) to 100 cc. C: Treat 1.3207 g.  $\text{As}_2\text{O}_3$  with  $\text{HNO}_3$  on a water bath, evap. nearly to dryness, take up with water, dil. to 1 l., dil. 10 cc. of this soln. to 1 l. 1 cc. = 0.01 mg. As. D: Dissolve 0.5 g. of neutral quinine-HCl in 10 cc. of distd. water, add 5 cc. of C and 10 cc. of B, and then 1 cc. of A, drop by drop with continuous stirring. The ppt. which first forms on adding A redissolves almost completely in a few min., giving a slightly cloudy and opalescent mixt. Dil. to 120 cc., mix, and filter through a filter previously washed with dil.  $\text{HNO}_3$  and then with water. This reagent can be kept for several months without changing. It gives a colloidal ppt. with  $\text{As}^V$ . Since it is satd. with quinine arsenomolybdate, it is extremely sensitive. By evapg. a few drops of an As soln. to dryness, treating the residue with a few drops of D, and observing the cloudiness by transmitted light with the help of magnifying glass, 0.00002 mg. As can be detected. The detn. can be carried out either by comparison with a series of standards or (preferably) by means of a colorimeter. The optimum As content is 0.008-0.035 mg. As, the standard being prepd. by adding 0.5 cc. of B to 2.5 cc. of C, then 2 cc. of water and 20 cc. of D. The solns. are allowed to stand 15 min. before comparison. Org. matter must be destroyed either with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , HCl and  $\text{KClO}_3$ , or by igniting with CaO or with MgO and  $\text{Mg}(\text{NO}_3)_2$ . Interfering metals are removed either by means of  $\text{H}_2\text{S}$  or by distg. the As as  $\text{AsCl}_3$ . In the absence of  $\text{H}_2\text{S}$  metals, make the soln. strongly acid, sat. with  $\text{H}_2\text{S}$ , cover, and let stand 24 hrs. Filter through asbestos, wash, dissolve with hot concd.  $\text{HNO}_3$  contg. Br water, evap. the filtrate and washings to dryness, and treat the residue as above. In the presence of  $\text{H}_2\text{S}$  metals, after de-

stroying org. matter with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  drive off most of the  $\text{H}_2\text{SO}_4$ , take up the residue (less than 1 cc.) with water, place in a 50-cc. glass-stoppered retort, add a little KCl (to fix  $\text{H}_2\text{SO}_4$ ), a little KBr, and a few crystals of hydrazine sulfate. The neck of the retort is slightly inclined upwards, and is connected to a vertical bulbéd tube which is drawn out to a fine opening dipping in a few cc. of water. Dist. nearly to dryness, let cool, add 1 cc. concd. HCl, dist. again nearly to dryness, and repeat this 3 or 4 times. If org. matter was destroyed by igniting with CaO or MgO, dissolve the mass in the least possible quantity of HCl and water, and dist. as above. If Sb or Hg is present, keep the temp. below  $115^\circ$  to prevent them from passing over into the distillate, as they would cause loss of As in the subsequent evapn. To the distillate add 20–30 cc. of water, 5 cc. concd.  $\text{HNO}_3$ , 5 cc. of Br water, and evap. to dryness on the water bath. Treat the As<sup>v</sup> as above. The method was tested on solns. of known As content, both alone and after addition of Cu, Hg, Sb, and org. matter (sugar, wine), and exceptionally good results were obtained (errors of 0.0001–0.0012 mg. on amts. of 0.00257–0.0429 mg. As).

A. P.-C.

Detection of traces of osmium by means of potassium thiocyanate. MAX HIRSCH. *Chem.-Zig.* 46, 390(1922).—To detect Os in a metal it may be dissolved in fuming  $\text{HNO}_3$  or fused with NaOH and  $\text{KNO}_3$  or  $\text{KClO}_4$  to form a sol. salt of perosmic acid. In the latter case, the melt should be dissolved in water and after the addition of concd.  $\text{HNO}_3$  carefully distd. Collect the volatile  $\text{OsO}_4$  in water, add a little HCl,  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  and test for Os with concd. KCNS soln. and ether or amyl alc. A distinct blue color will be obtained if the acid soln. contains 1 part of  $\text{OsO}_4$  in 1 million of water. In the tests a small vol. of the Os soln. was treated with 5 cc. of concd. KCNS and 3 cc. of ether or amyl alc.

W. T. H.

Complete analysis of oxide mixtures formed in the refining of lead. W. STAHL. *Chem.-Zig.* 46, 409–10(1922).—Treat 1 g. of dry powder with 30 cc. concd.  $\text{HNO}_3$  and evap. to dryness. Add a little  $\text{HNO}_3$ , dil., and filter off the more or less impure metastannic acid, washing with hot, dil.  $\text{NH}_4\text{NO}_3$  soln. Fuse the dried residue with a mixt. of  $\text{Na}_2\text{CO}_3$  and S in a porcelain crucible, ext. the melt with a little cold water, and filter off the insol. sulfides, washing with dil.  $\text{Na}_2\text{S}$  soln. This filtrate contains As, Sb and Sn as sol. thio salts. Into the dil.  $\text{HNO}_3$  soln. obtained from the original treatment of the sample pass  $\text{H}_2\text{S}$  and ppt. the members of the Cu group. The filtrate from this ppt. will contain the greater part of the Zn together with Fe and Ni. It may be called soln.  $\alpha$ . Digest the sulfide ppt. with hot concd.  $\text{Na}_2\text{S}$  soln. to recover small quantities of As, Sb and Sn and combine the soln. with that obtained from the fusion with  $\text{Na}_2\text{CO}_3$  and S. The undissolved ppt. may contain PbS,  $\text{Ag}_2\text{S}$ , CuS,  $\text{Bi}_2\text{S}_3$ , CdS and possibly a little ZnS. Dissolve these sulfides in  $\text{HNO}_3$ , filter off any residue, ignite the filter and add the ash to the  $\text{HNO}_3$  soln. From the  $\text{HNO}_3$  soln. boil off nitrous oxides, nearly neutralize with  $\text{NH}_3$  and again sat. with  $\text{H}_2\text{S}$ . In this case any Zn that was pptd. the first time, will remain in soln. and after filtering should be added to soln.  $\alpha$ . Det. Pb, Ag, Cu, Bi, Cd, Fe, Zn and Ni as described in a former paper (*C. A.* 15, 3955). Det. Ag by fire assay. To the alk. soln. of thio salts add dil.  $\text{H}_2\text{SO}_4$  to ppt. sulfides of As, Sb and Sn, filter and wash with  $\text{NH}_4\text{NO}_3$  and very dil.  $\text{HNO}_3$  soln. Redissolve the sulfides in freshly prepd., hot  $(\text{NH}_4)_2\text{S}$  soln. and evap. the soln. to pasty consistency. Add a little concd. HCl and some  $\text{KClO}_4$  to dissolve the sulfides, using a reflux condenser to prevent loss of Sn or As. Add tartaric acid and  $\text{NH}_4\text{OH}$  to the soln. of chlorides and ppt. the As as  $\text{MgNH}_4\text{AsO}_4$  (cf. *C. A.* 15, 3955). In the filtrate from this pptn., ppt. the As and Sn as sulfides again by  $\text{H}_2\text{S}$  in acid soln. Filter, wash, and dissolve in a little  $\text{Na}_2\text{S}$  soln. Decolorize the soln. by treatment with  $\text{Na}_2\text{O}_2$  and add alc. to ppt.  $\text{NaSbO}_3$ . After 12 hrs., filter and digest the ppt. first with 50% alc. and a little  $\text{Na}_2\text{CO}_3$  soln., then with 75% alc. and a few drops of soda soln. until a filtrate is obtained which

will give no test for Sn with  $H_2S$ . Dissolve the  $NaSbO_3$  in a mixt. of 2  $N$   $HCl$  and 5–10% tartaric acid soln. and det. the Sb as  $Sb_2O_3$  as already described (C. A. 15, 3955). Boil off the alc. from the filtrate contg. the Sn, make acid and introduce  $H_2S$  to ppt.  $SnS_2$ . Ignite and weigh as  $SnO_2$  with the usual precautions. W. T. H.

**Zinc separations with ammonium phosphate.** G. LUFF. *Chem.-Ztg.* 46, 365–6 (1922); cf. C. A. 15, 365–6.—Voigt's method for sepg. Mg and Zn which depends upon the fact that  $ZnNH_4PO_4$  is sol. in  $NH_4OH$  soln. whereas  $MgNH_4PO_4$  is not, was tried and found to be reliable. In an atm. of H and a soln. contg. 25% concd.  $NH_3$  soln. and 20 g.  $NH_4Cl$  it was found possible to ppt. 0.04 to 0.15 g. Mn as  $MnNH_4PO_4$  in the presence of 0.2 to 0.04 g. of Zn, which does not form an insol. phosphate under these conditions. The pptn. of Fe as phosphate in an ammoniacal soln. contg. Zn was not entirely successful but in a soln. contg. 20% glacial AcOH it was possible to get good results and similarly it was found possible to ppt. pure  $AlPO_4$  in AcOH soln. contg. Zn. In an ammoniacal soln., therefore, it is possible to ppt.  $MgNH_4PO_4$  and  $MnNH_4PO_4$  free from  $ZnNH_4PO_4$  and in AcOH soln. it is possible to ppt.  $FePO_4$  and  $AlPO_4$  free from  $ZnNH_4PO_4$ . W. T. H.

**Detection and determination of small quantities of nickel and cobalt in silicate rocks.** O. HACKL. *Chem.-Ztg.* 46, 385–6 (1922).—In most of the standard works on rock analysis little attention is paid to the dimethylglyoxime test for Ni, to the nitroso- $\beta$ -naphthol test for Co or to the Vogel test for Co with thiocyanate. This paper shows how these tests may be easily applied to rock analysis. W. T. H.

**Separation of palladium and platinum by means of dimethylglyoxime.** C. W. DAVIS. *Bur. Mines, Repts. Investigations* 1922, No. 2351, 2 pp.—Treatment with  $HNO_3$  does not give a satisfactory sepn. of Pd and Pt but if a faintly acid chloride soln. is treated at room temp. with dimethylglyoxime soln. the Pd is pptd. completely and with no Pt. The procedure is as follows: Dissolve the weighed metals in a little *aqua regia*. Evap. to dryness, moisten the residue with a drop of  $HCl$  soln., dil. with cold water and add dimethylglyoxime with const. stirring until no more ppt. is formed. After a few min., filter off the voluminous Pd ppt., wash well with cold water and ignite first in air and finally in H to get pure Pd. The method was tested with quantities of each metal ranging from 0.15 to 11 mg. and the greatest divergence in 5 analyses was 0.03 mg. W. T. H.

**Glacial acetic acid method for determining uranium in carnotite.** W. W. SCOTT. *J. Ind. Eng. Chem.* 14, 531–2 (1922).—Digest 0.5 g. carnotite with 20–40 cc. of 7.5  $N$   $HNO_3$ , boil gently, evap. to dryness, bake the residue a few min. and then heat with 25 cc. of a mixt. contg. 20 pts. AcOH to 5 pts.  $HNO_3$ . If the ratio of AcOH to  $HNO_3$  is more than 10:1, V is not dissolved appreciably. Filter, evap. the soln. to dryness and repeat the AcOH treatment. Filter, evap., bake and dissolve this time in 50 cc. of 3  $N$   $HNO_3$ . Nearly neutralize with  $NH_4OH$ , add an excess of  $(NH_4)_2CO_3$  and filter off the Fe and Al hydroxides. To the filtrate add  $HNO_3$ , boil off  $CO_2$  and ppt. the U as  $(NH_4)_2U_2O_7$  by adding  $NH_4OH$ . Filter, wash with 2%  $NH_4NO_3$  soln., ignite and weigh as  $U_3O_8$ . W. T. H.

**The determination of cobalt in steel.** ALOIS EDER. *Chem.-Ztg.* 46, 430 (1922).—Dissolve 2 g. of metal in 40 cc. of 3  $N$   $H_2SO_4$  and oxidize the Fe by careful addition of  $HNO_3$ , avoiding an excess. Evap. to sirupy consistency, dil. to 200 cc. and slowly add  $ZnO$  suspension until all the  $Fe^{+++}$  is pptd. Cool, dil. to exactly 500 cc., filter and take  $1/2$  of the filtrate. Add 7 cc. of concd.  $HCl$ , evap. to about 100 cc., dil. to about 150 cc., heat to boiling and slowly add a freshly prepd., hot soln. of nitroso- $\beta$ -naphthol in 50% AcOH. After about 2 hrs., during which time the contents of the flask should be frequently shaken, filter and wash the Co ppt. with cold 2  $N$   $HCl$ , hot 2  $N$   $HCl$  and finally with hot water. Sprinkle a little oxalic acid on the filter and ignite carefully to  $Co_2O_3$  in a weighed porcelain crucible. W. T. H.

**The determination of carbon monoxide in blast-furnace gas by combustion.** TH. KALETA. *Chem.-Ztg.* **46**, 430(1922).—Usually the CO is detd. by absorption with  $\text{Cu}_2\text{Cl}_2$ , but if the soln. is not fresh some will escape absorption. In blast-furnace gas there is rarely an appreciable amt. of  $\text{CH}_4$  present. It is recommended, therefore, and a suitable app. is described, first to absorb the  $\text{CO}_2$  of the gas, mix the residue with an excess of  $\text{O}_2$ , ignite by means of a glowing Pt wire electrically heated, measure the contraction and absorb the  $\text{CO}_2$  formed from the CO. If it is desired to know the  $\text{CH}_4$  content, it is necessary to absorb the unused  $\text{O}_2$  with P or with pyrogallol. W. T. H.

**Quantitative micro-analysis of organic substances.** R. CORNUBERT. *Rev. gen. sci.* **33**, 198-204(1922).—In a previous paper (*C. A.* **14**, 3042) the work of Pregl was described; in this paper the work of Dubsy (*C. A.* **13**, 822) is discussed and his methods of microelementary analysis are compared with those of Pregl. The micro-Carius method of Donau is described and a short history given of methods used in elementary org. analysis from 1781 to the present time. W. T. H.

**The kjeldahlization of mononitrophenols, mononitrobenzoic acids, and mononitrocinamic acids.** B. M. MARGOSCHES AND ERWIN VOGEL. *Ber.* **55B**, 1380-9 (1922).—The N content of *o*-nitrophenol and of *o*-nitrobenzoic acid can be detd. by the Kjeldahl method without the use of catalyzer. Treatment with concd.  $\text{H}_2\text{SO}_4$  alone gave practically the same values as when  $\text{K}_2\text{SO}_4$  was added in the Gunning modification of the Kjeldahl method. With the *m* and *p* derivs., the results were lower when  $\text{K}_2\text{SO}_4$  was added than when  $\text{H}_2\text{SO}_4$  was used alone. With  $\text{CuO}$  and  $\text{HgO}$  as catalyzers, better results were obtained and the addition of  $\text{K}_2\text{SO}_4$  was found to be detrimental with  $\text{HgO}$ ; the results were always a little low with the *m* and *p* derivs. With *p*-nitrobenzoic acid some of the N was given off as a volatile product which could be absorbed in phenol and the N content obtained by the Kjeldahl process using  $\text{CuO}$  as catalyzer. With *p*-nitrophenol the reaction is more complicated and some N is always lost. With the mononitrocinamic acids the results obtained by the Gunning method were fairly accurate. In the decompn. by  $\text{H}_2\text{SO}_4$ , two stages were observed. With the *o* compds. the first period was characterized by the formation of a nearly black soln.; during this period the greater part of the N was obtained as  $\text{NH}_4\text{HSO}_4$  and the remainder when the soln. was decolorized. With the *p* compds. the soln. did not become black but merely brown and during this stage practically no N was converted into  $\text{NH}_4\text{HSO}_4$ . Expts. in which  $\text{Li}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4$  was used instead of  $\text{K}_2\text{SO}_4$  in the decompn., showed that the K salt is more effective. W. T. H.

**The determination of guanidine.** A. H. DODD. *J. Soc. Chem. Ind.* **41**, 145-7T (1922).—When guanidine salts are made from guanylurea salt or from dicyanodiamide the ordinary picrate method of analysis cannot be used because insol. ppts. are obtained with guanylurea salts but a sepn. can be effected more or less successfully on the basis of the soly. of guanylurea picrate in dil.  $\text{NaOH}$ . A series of expts. is described in the analysis of guanidine malonate, nitrate, carbonate and nitrate showing how the analysis is affected by varying the conditions and the conclusion drawn that each analyst must det. for himself the best conditions for pptg. guanidine according to the salt used and the precipitant. W. T. H.

**The determination of aromatic hydrocarbons in distillation fractions of mineral oils.** H. I. WATERMAN AND J. N. J. PERQUIN. *Rec. trav. chim.* **41**, 192-8(1922).—Tizard and Marshall have proposed a test for the detection of aromatic hydrocarbons (*C. A.* **15**, 1867) which depends upon the lowering of the "aniline point." A mixt. of equal parts hydrocarbon and aniline is tested to see at what temp. 2 phases begin to sep. This test is applicable only to materials which do not contain any unsatd. non-aromatic hydrocarbons. It was tried on high boiling fractions of a Sumatra oil, and of a Borneo oil and it was found that the position of the aniline point varies with

different fractions of each oil and that the lowering is nearly proportional to the % of aromatic hydrocarbons present but that the same % by wt. of benzene, naphthalene and phenanthrene do not give the same lowering.

E. J. WITZEMANN

The detection and determination of saccharin. J. POPPER. *Natuurwetenschappelijke Tijdschrift* 1921; *Ann. chim. anal. chim. appl.* [2] 4, 157-8(1922).—P. suggests detg. saccharin by detg. N by the Kjeldahl method in the material extd. by  $\text{Et}_2\text{O}$  in the usual manner. If traces only are present, the distillate can be nesslerized. For its detection, evap. off the  $\text{Et}_2\text{O}$ , heat the residue to redness in the presence of  $\text{CaO}$ , passing a current of air through the tube and through a few cc. of water, and nesslerizing. The residue after evapg. off the  $\text{Et}_2\text{O}$  can also be heated with metallic Na to transform the N into NaCN, which is detected either by pptg. as Prussian blue or by transforming into NaCNS and adding  $\text{Fe}^{+++}$ . The latter can be used for the quant. detn. of the saccharin.

A. P.-C.

Chromic thiocyanates. III. Methods of analysis (BJERRUM) 6. Impurities in synthetic potassium nitrate (determination of  $\text{KClO}_4$ ) (JUNK) 24. Compounds of iodine with the components of starch (EULER, MYRBACK) 28.

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THOMSON, J. J.: *Rays of Positive Electricity and Application to Chemical Analyses* 2nd. Ed. London: Longmans, Green & Co. 237 pp. 16s. Reviewed in *Nature* 109, 671(1922).

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## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

Orpiment of Swedish origin. I. D. WALLERIUS. *Geol. För. Förh.* 43, 671-2 (1921).—A 20-g. piece of orpiment from the Svartvik mine, Svärdsjö, Dalarne, Sweden, dates back to approx. 1821. No trace of the associated rock is visible, but the mineral contains Pb.

W. SÖGERBLOM

Observations suggested by Wallerius' note on orpiment of Swedish origin. N. ZENZÉN. *Geol. För. Förh.* 44, 172-3(1922); Studies relating to the Mining College mineral collection. V. The supposed discovery of arsenolite and orpiment in Swedish ores. N. ZENZÉN, H. G. SÖDERBAUM AND HJ. SJÖGREN. *Arkiv. Kemi. Mineral. Geol.* 8, No. 20, 4 pp.(1922); cf. preceding abstr.—The only known specimen of orpiment from the Rotendal mines is in the Mining College, having been collected by Tilas in 1737. Being optically isotropic, with high  $n$ , and giving Zn reactions, it is clearly sphalerite. The arsenolite from Löfåsen mines, Dalarne, is a decomn. product of arsenopyrite caused by fire in the mines. The so-called orpiment and realgar from Löfåsen are products obtained by roasting ores contg. As sulfides. The orpiment from the Svartvik mine, mentioned by Wallerius is litharge probably made by driving off the Pb from argentiferous galenite. Other instances of litharge labelled as orpiment occur at the Royal Museum.

W. SÖGERBLOM

A new occurrence of cristobalite in California. A. F. ROGERS. *J. Geology* 30,

211-6(1922).—In obsidian from San Bernardino Co. ( $n = 1.483, \pm 0.003$ ), are rod-shaped crystallites in parallel lines, and spherulites 5-25 mm. in diam. The solid portions of the spherulites consist of orthoclase and cristobalite, in fibrous aggregates which on microscopic examn. prove to be intergrowths. Other minerals identified include tridymite, opal, magnetite and fayalite. The cristobalite was formed at a high temp. and as the temp. became lower, tridymite appeared, and at about the same time fayalite and magnetite. The opal is the only mineral formed by ordinary solns. W. F. H.

**Nature and chemical composition of a mineral containing cobalt found at Katanga.** A. SCHORP. *Bull. soc. chim. Belg.* 30, 207-12(1921).—A colloidal mineral, allied to heterogenite (cf. Frenzel, *J. prakt. Chem.* [2] 5, 404) and schulzenite (cf. Maertens, *Ades Soc. Sci. Chili.* 5, 87-8(1895)) and resembling lustrous anthracite in appearance, has been found embedded in malachite and chrysocolla. Its composition is estd. to be  $3\text{Co}_3\text{O}_4 \cdot \text{CoO} \cdot \text{CuO} \cdot 7\text{H}_2\text{O}$ . J. C. H.

**Presence of zinc in malachite from Chessy.** C. PERRIER. *Atti. accad. Lincei* 30, i, 309-11(1921).—It has been shown that rosasite, to which Lovisato attributed the formula  $2\text{CuO} \cdot 3\text{CuCO}_3 \cdot 5\text{ZnCO}_3$ , is in reality a basic Zn-Cu carbonate with the constitution  $(\text{Zn}, \text{Cu})\text{CO}_3 \cdot \text{Cu}(\text{OH})_2$ , which is analogous to that of malachite. Thus, rosasite resembles aurichalcite, in which also part of the Zn is replaced by copper. Analysis of a sample of pure, crystd. malachite from Chessy gives the results:  $\text{H}_2\text{O}$  8.36,  $\text{CO}_2$  19.87,  $\text{CuO}$  71.31,  $\text{ZnO}$  0.45,  $\text{Fe}_2\text{O}_3$  0.04,  $\text{PbO}$  trace, residue trace, total 100.03. In mol. proportions, these figures correspond with  $1.02 \text{H}_2\text{O} : 1.00 \text{CO}_2 : 1.99(\text{CuO} + \text{ZnO})$ , so that the sample represents a typical malachite in which a small, but appreciable, proportion of the Cu is replaced by Zn. J. C. S.

**Velardeñite from a locality in Tulare County, California.** E. V. SHANNON. *Proc. U. S. Nat. Museum* 60, 1-4(1922).—The material is coarse granular, olive-green to black, but under the microscope colorless, with  $n_s \omega = 1.657, \epsilon = 1.653$ . Anal. gave:  $\text{SiO}_2$  27.88,  $\text{Al}_2\text{O}_3$  25.52,  $\text{Fe}_2\text{O}_3$  1.59,  $\text{FeO}$  0.43,  $\text{MgO}$  4.18,  $\text{CaO}$  40.86,  $\text{H}_2\text{O}$  0.34, sum 100.80 %. The formula is:  $14\text{CaO} \cdot 2\text{MgO} \cdot 5\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ , corresponding to velardeñite: äkermanite = 5:2, and being close to that of material from Velardeña, Mex.

L. W. R.

**Crocidolite from eastern Pennsylvania.** E. T. WHERRY AND E. V. SHANNON. *J. Wash. Acad. Sci.* 12, 242-4(1922).—Crocidolite is found in eastern Pa. as impregnations and coatings on Pre-Cambrian gneisses and Triassic diabase and sediments. It was probably deposited by hydrothermal solns. from the Triassic magma. Much of the material is cryptocryst.; at some localities fibrous and bladed material gave  $\alpha$  1.64-1.65,  $\beta$  1.65,  $\gamma$  1.66, pleochroism X yellow, Y green, Z blue. Anal. by S. gave:  $\text{SiO}_2$  51.62,  $\text{Al}_2\text{O}_3$  0.92,  $\text{Fe}_2\text{O}_3$  18.36,  $\text{Ti}_2\text{O}_3$  2.27,  $\text{FeO}$  10.93,  $\text{MgO}$  5.92,  $\text{CaO}$  0.48,  $\text{Na}_2\text{O}$  5.62,  $\text{K}_2\text{O}$  0.66,  $\text{H}_2\text{O}$  3.61, sum 100.39%; formula,  $\text{H}_2\text{O} \cdot \text{Na}_2\text{O} \cdot \text{MgO} \cdot \text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$ .

EDW. F. HOLDEN

**Handbook and descriptive catalog of the collections of gems and precious stones in the U. S. National Museum.** G. P. MERRILL, MARGARET W. MOOREY AND E. T. WHERRY. *Smithsonian Inst. Nat. Mus. Bull.* 118, 218 pp.(1922).—Comprises: I.—History and arrangement of the collections. II.—Chem., physical and especially the optical characters. III.—A descriptive catalog of the collections, filling 111 pp. "Under each mineral or gem is given in tabular form some of the more striking qualities of a descriptive or determinative nature, followed by remarks on mode of occurrence and such other miscellaneous information as it is thought would be of value. In the catalog proper the material is arranged in the following order: name, locality, cut, color, wt., measurements and catalog no. Wts. are given in the newly introduced metro-carats." The specimens are listed by localities, and under each locality are arranged generally in the order of decreasing wts. IV.—A catalog of supplemental collections. The occurrence and association of precious stones, particularly the diamond-

bearing rocks of S. Africa and the granite-pegmatites of the Appalachian and Californian regions are described. Appendices include data on synonymous, trade and miner's names for gems and their mineralogical equivalents, industrial uses, tables for the identification of gems, statistics of production and bibliography.

L. W. RIGGS

**Notes on white chlorites.** E. V. SHANNON AND F. T. WHERRY. *J. Wash. Acad. Sci.* 12, 239-41 (1922).—New analyses of white chlorites, called colerainite, sheridanite, etc., gave:

	1.	2.	3.
SiO <sub>2</sub>	28.10	36.70	27.78
Al <sub>2</sub> O <sub>3</sub>	26.20	10.38	24.30
Fe <sub>2</sub> O <sub>3</sub>	1.66	1.22	0.35
FeO	none	trace	1.43
CaO	trace	0.86	trace
MnO	trace	trace	none
MgO	30.36	36.44	32.71
H <sub>2</sub> O+	14.00	13.80	13.01
H <sub>2</sub> O—	0.56	1.06	0.06
sum	100.88	100.46	99.64
$\alpha$	1.562	1.555	1.576
$\beta$	1.562	1.560	1.576
$\gamma$	1.576	1.560	1.589
2E	0°	30°	small
sign	+	—	+

1. Brinton's Quarry, Pa. 2. Nottingham, Pa. 3. Wyoming. White chlorite from Sylmar, Pa. showed the forms: 001, 010, 110, 112, 011, 043,  $\bar{1}11$ , 132,  $\bar{1}01$ ,  $\bar{1}34$ . The Pa. chlorites were formed by the action of Mg-bearing waters on albite-pegmatite.

EDW. F. HOLDEN

**The minerals of the redeemed territories.** GAETANO CASTELLI. *Rass. min.* 56, 60-2 (1922).—A detailed outline of the available mineral deposits in the regions of Trentino, Alto Adige and Venezia Giulia recently acquired by Italy. The important deposits include Cu, Ag, Hg and Zn ores, chalcopyrite, galenite, sphalerite, pyrite, magnetite, Fe silicates, malachite, azurite, wolframite, lignite and bituminous shale.

C. C. DAVIS

**The metalliferous deposits surrounding the granites of the Arbus-Villacidro region in Sardinia.** EDOARDO SANNA. *Rass. min.* 56, 59-60 (1922).—The granitic plateau of Arbus extends to Villacidro, where it is in contact with Silurian porphyrite and diorite, with parallel interposed veins of Pb and Zn. The northern contacts at Gennamari Ingurtosi contain a preponderance of galenite, with increase of sphalerite as the veins recede from the granites. At S'Acqua Bona and Nieddoris are complex veins of the sulfides and arsenides of Fe, Pb, Zn, Cu and Ni. The southern contacts are similar, but at Macciurru contain veins of galenite parallel to the eruptive rock, and at Permessu Canale Serci mixed sulfides of Pb and Zn and arsenides of Fe. All these deposits can be successfully exploited. In the veins of Macciurru 100 tons of galenite contg. 67% Pb and 50 kg. of Ag have been extd.

C. C. DAVIS

**Notes on zinc and lead.** J. COGGIN BROWN. *Bull. Indian Ind. and Labour* 1922, No. 19, 80 pp.—The uses and marketing of Zn and Pb, valuation of the ores, and statistics on world supply, production, and Indian imports and exports are given. The Indian ores are chiefly sphalerite and galenite, the Bawdwin mines of the North Shan States are important.

EDW. F. HOLDEN

**The primary zones of Cornish mines.** F. H. DAVISON. *Geol. Mag.* 58, 505-12 (1921).—The primary minerals of the Cornish lodes occur in zones which change their

character in depth, Cu minerals giving place to cassiterite, and chlorite to tourmaline. The characters of the zones and their mineralization are described. S. G. G.

**Notes on the banded chromite ore from Akaishi mine in the province of Iyo, Japan.** TAKAO KARŌ. *J. Geol. Soc. Tokyo* 28, 13-8(1921).—The deposits occur in a dunite intrusive in mica schists. The ore shows a banded texture, or sometimes a fluxion structure. The chromite is always of the earliest period of crystn., and shows magmatic corrosion. The chromite crystals in the black layers are crushed or granulated along the margins and cracks; the crushed off grains also showing corrosion. The banded ore was probably formed by a flowing motion of the crystg. dunite, in which settling of chromite crystals was going on. S. G. GORDON

**Geology and mining of mica.** J. VOLNEY LEWIS. *Eng. Mining J.-Press* 113, 856-64(1922).—Muscovite occurs chiefly in pegmatite, while phlogopite in Canada is found in a pyroxene-calcite-apatite rock. The principal producers of mica are India, U. S. (N. C., N. H., and Va.), and Canada. Mica mining is usually crude.

EDW. F. HOLDEN

**Garnet.** RAYMOND B. LADOO. U. S. Bur. of Mines, *Repts. of Investigations* No. 2347, 16 pp.(1922).—This paper gives a general description of garnets, their geological occurrence, localities (N. Y., N. H., N. C., Conn., Pa., Ga., Va., Spain, Labrador), statistics as to production (from 1910-18, U. S. production was four to six thousand tons/yr., the value increased from 113 to 248 thousand dollars, N. Y. being the largest producer), methods of mining and milling tests, uses (abrasives) and a bibliography.

EDW. F. HOLDEN

**The new corundum industry in the Zoutpansberg district of the northern Transvaal.** A. L. HALL. *S. African J. Ind.* 5, 153-9(1922); cf. *C. A.* 15, 3599.—In northern Transvaal corundum is associated with feldspar and mica and its greater sp. gr. allows ready sepn. therefrom. Milling operations consist of crushing, concg. and grading. 15 grades of grain corundum vary from 10 to 100 mesh per inch in size and have greenish gray color. Analyses of several grades show:  $Al_2O_3$ , 94.9-96.5,  $SiO_2$ , 1.10-2.30,  $Fe_2O_3$ , 0.95-1.75,  $TiO_2$  +  $TiO$  0.15,  $H_2O$  1.25-2.20%. It has high cutting efficiency and can compete with artificial abrasives.

W. H. BOYNTON

**Sodium sulfates in Sicily.** EMILIO CORTESE. *Rass. min.* 56, 57-9(1922).—Two deposits rich in  $Na_2SO_4$  near Bompensiere, and at Monte Sambuco near Calascibetta, are now under development. The former is chiefly *glauuberite*, with deposits, in the upper beds, of pure  $Na_2SO_4$ . The  $CaSO_4$  and  $Na_2SO_4$  are sepd., by virtue of their differing soly. through treatment with warm  $H_2O$ . Small amts. of  $NaCl$  also are present. The second contains several salts, and may be called collectively polyhalite, 3 analyses showing:  $Na_2O$  8.45, 2.85, 1.65;  $K_2O$  8.94, 2.81, 5.64;  $CaO$  0.86, 0.73, 0.80;  $MgO$  12.76, 14.14, 13.72;  $Cl$  6.86, 5.74, 1.84;  $SO_4$  41.16, 47.26, 48.69.

C. C. DAVIS

**Possible cause of the red color of potash salts.** W. C. PHALEN. *Science* 55, 479-80(1922).—Studies by W. W. Browne (*Bur. of Fisheries Doc.* 896, 27-8(1920)) indicate that the red color of salt fish is due to microorganisms which probably originated in the sea-salt used for curing the fish. These organisms grow only in brines contg. 15% or more salt, and best at temps. of 50° to 60°. Sunlight does not destroy them. P. suggests that possibly similar causes may have been operative in geological ages when K salts were laid down.

W. C. EBAUGH

**The extent and nature of the "reh" deposits of the United Provinces.** F. R. WATSON AND K. C. MUKERJEE. *J. Indian Ind. Labour* 2, 13-28(1922).—It is estd. that the "reh" deposits (efflorescent soils contg. Na carbonate and sulfate) in the United Provinces would yield by scraping 4,888,000 tons  $Na_2CO_3$  annually, enough to meet all domestic demands.

EDW. F. HOLDEN

**Coal in the northern Waterberg.** T. G. TREVOR AND A. L. DU TOIT. *S. African*



*J. Ind.* 5, 164-70(1922).—The Waterberg district contains coal deposits at depths of 30-70 ft. Analyses from 7 seams show high volatile high ash compn. Samples taken below the 300-ft. level correspond with ordinary Transvaal and Natal qualities, while those from the upper seams are more bituminous than any previously worked in the country. This coal area is worthless until railway communication is secured.

W. H. BOYNTON

**Phosphorus in Californian petroleum.** CHASE PALMER. *Econ. Geol.* 17, 100-4 (1922).—Californian heavy oils contg. N bases have been found to contain also P, which is considered another link in the chain of evidence that this petroleum is of animal origin.

CHAS. W. COOK

**Origin of Alberta tar sands.** A. F. A. COVNE. *Petroleum Age* 9, No. 8, 22-3 (1922).—The tar deposits are due to an upwelling of petroleum into the McMurray syncline.

R. L. SIBLEY

**Development of pressure in magmas as a result of crystallization.** GEO. W. MOREY. *J. Wash. Acad. Sci.* 12, 219-30(1922).—"When a system composed of volatile and non-volatile components such as  $H_2O$  and  $KNO_3$  is cooled, crystn. will take place at a temp. lower than the freezing point of the pure non-volatile salt by an amt. corresponding to the amt. of volatile material present, and the corresponding 3-phase pressure increases rapidly as the temp. is lowered from the m. p. of the salt. This increase is rapid whether measured in terms of the decrease in temp. of the 3-phase equil. or in terms of the content of volatile material in the soln. From the latter fact it follows that in systems of the type of magmas, in which the non-volatile material is composed of such substances as the silicates, and in which the pressure required to retain any considerable proportion of  $H_2O$  in soln. must be large, a comparatively small amt. of crystn. will result in a large increase in pressure. When a magma containing  $H_2O$  cools, with consequent crystn. and development of high pressure, under an incompetent crust, a release of pressure will take place, which may be catastrophic in violence or take the form of a succession of mildly explosive outbursts. In case the magma cools under a competent crust the pressure will rise to a max., then decrease, probably without at any time showing critical phenomena."

L. W. RIGGS

**The metasomatic processes in silicate rocks.** V. M. GOLDSCHMIDT. *Econ. Geol.* 17, 105-23; *Naturwissenschaften* 10, 145-52(1922); cf. *C. A.* 16, 888.—G. defines metasomatism as "a process of alteration which involves enrichment of the rock by new substances brought in from the outside. Such enrichment takes place by definite chem. reactions between the original minerals and the enriching substances." He discusses the classification of the metasomatism of silicate and silica rocks and also gives a physico-chem. theory of metasomatism involving the principle of minimum concn. (or minimum vapor pressure).

CHAS. W. COOK

**The reaction principle in petrogenesis.** N. L. BOWEN. *J. Geology* 30, 177-98 (1922).—In the past too great emphasis has been placed on eutectic phenomena in the crystn. of molten magmas. It is pointed out that another relation between crystals and liquid, called the reaction relation, is very common in silicates. The ordinary solid soln. series such as the plagioclases may be regarded as a continuous reaction series because during crystn. each member is produced from an earlier member by reaction with the liquid, the variation of compn. being continuous. There are also discontinuous reaction series with related characters but with discontinuous changes of compn. such as olivine-pyroxene-amphibole-mica.

W. F. H.

**The origin of gumbotil.** G. F. KAY AND J. N. PRARCE. *J. Geol.* 28, 89-125 (1920).—The aim of this paper has been to show by field and lab. evidence that the gumbotils on Nebraskan, Kansan, and Illinoian glacial tills are the results of chem. weathering of the drift and furnish good criteria for differentiating the older drifts. It is recog-

nized that wind action, freezing and thawing, burrowing of animals and slope wash have also contributed to their formation. W. F. HUNT

Some colloidal properties of Pleistocene clays and their bearing on the chemical theory of the formation of the gumbotil. J. N. PEARCE AND L. B. MILLER. *J. Phys. Chem.* 26, 1-24 (1922).—The authors discuss the geological and chem. evidence in support of the theory of Khy and Pearce (preceding abstract). This assumes that, following the laying down of each original drift, a long period elapsed during which chem. weathering and leaching took place; that the upper layers are the residua left by these processes. After a time diastrophic movements occurred, and erosion then developed the topography existing at the ends of the interglacial periods. L. W. RIGGS

The magnesian group of igneous rocks. F. DIXEY. *Geol. Mag.* 58, 485-93 (1921).—After briefly describing the group and magnesian provinces, the writer discusses their origin and relation to other rocks. S. G. GORDON

The alkali rocks of the Serra do Gericino to the northwest of Rio de Janeiro, and the resemblance between eruptive rocks of Brazil and those of South Africa. H. A. BROUWER. *Proc. Acad. Sci. Amsterdam* 23, 1241-55 (1921).—The alkali rocks occur in old gneisses and include: granular rocks, foyaites, alkali-syenites, umptekites, and pulaskites; dike rocks, tinguaite, sölvbergite, trachytes, nepheline-syenite-aplites, and alkali-syenite-porphyrries. The similarity in every period between igneous rocks of Brazil and South Africa is striking, and suggests that there are grounds for the theory that the continents were sepd. by horizontal movements. EDW. F. HOLDEN

The composition and the xenoliths of the lava dome of the Galunggung (West Java). H. A. BROUWER. *Proc. Acad. Sci. Amsterdam* 23, 1234-40 (1921).—During an eruption of the Galunggung in 1918 a lava dome formed in the crater. The lava is a brownish red, porous, hypersthene-augite andesite, with phenocrysts of zonal plagioclase (bytownite). The xenoliths range from varieties containing only plagioclase and amphibole to rocks with plagioclase, pyroxene, and ore, with also older andesites. The first type of xenoliths had not completely crystd. when taken up in the lava. The amphiboles show a resorption rim where they border the glass, having been stable until the time of eruption, when with decreasing pressure they became unstable and in the period before final solidification augite crystd. out. Therefore, the proportion of augite to amphibole varies according to the length of time when resorption of amphibole could occur; this depends on the depth of origin of the xenoliths. EDW. F. HOLDEN

A leucite rock, vulsinitic vicoite, from Utsuryōtō Island in the Sea of Japan. SHITARŌ TSUBOI. *J. Geol. Soc. Tokyo* 27, 91-103 (1920).—Utsuryōtō Island is composed principally of alk. trachytic rocks covering older basaltic bodies. The vulsinitic vicoite is a porphyritic rock, consisting of phenocrysts of sanidine and labradorite, hornblende and augite, and rarely of anhedral olivine, in a gray aphanitic groundmass composed of orthoclase, plagioclase, and leucite. An analysis (by Ōhashi):  $\text{SiO}_2$  57.91,  $\text{Al}_2\text{O}_3$  18.22,  $\text{Fe}_2\text{O}_3$  1.90,  $\text{FeO}$  3.20,  $\text{MgO}$  1.01,  $\text{CaO}$  3.58,  $\text{Na}_2\text{O}$  4.98,  $\text{K}_2\text{O}$  6.69,  $+\text{H}_2\text{O}$  0.82,  $-\text{H}_2\text{O}$  0.38,  $\text{CO}_2$  none,  $\text{TiO}_2$  0.65,  $\text{ZrO}_2$  0.07,  $\text{P}_2\text{O}_5$  0.48,  $\text{SO}_2$  none,  $\text{MnO}$  0.27,  $\text{BaO}$  none, sum 99.98%. The chem. factors controlling the formation of leucite are discussed. S. G. GORDON

Detection and determination of small quantities of nickel and cobalt in silicate rocks (HACKL) 7. Haloes and earth history (JOLY) 3. Oil in the Quadrant formation in Montana (FREEMAN) 22.

BEYSCHLAG, FRANZ, KRUSCH, PAUL, and VOGT, HERMAN L. *Die Lagerstätten der nutzbaren Mineralien und Gesteine nach Form, Inhalt und Entstehung dargestellt.* Band II. Stuttgart: F. Enke.

CRONSHAW, H. B.: *Silver Ores*. London: John Murray. 152 pp. 6sh. Reviewed in *Chem. Eng. Mining Rev.* 14, 237(1922).

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### 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

**Mt. Lyell concentrating plant.** ANON. *Chem. Eng. Mining Rev.* 14, 213-4(1922).—The flowsheet of the plant is given in considerable detail for an ore consisting of 6% Cu. This is crushed to about 4-in. size and screened, the coarse material is hand-sorted, the waste rejected and the coarse sent to the smelter. The fines from the screening operation is crushed to 1.5 in. by a Bigelow crusher then by rolls to 1/8 in. The coarse material is jigged and the slimes washed out are sent to a flotation system. W. A. M.

**Gold, silver, copper, lead and zinc in the Eastern States in 1921.** J. P. DUNLOP. U. S. Geol. Survey, *Mineral Resources of U. S.* 1921, Pt. I, 7-13(preprint No. 2, publ. May 12, 1922). E. J. C.

**Copper in 1920.** H. A. C. JENISON. U. S. Geol. Survey, *Mineral Resources of the U. S.* 1920, Pt. I, 451-503(preprint No. 26, publ. May 16, 1922). E. J. C.

**Heap leaching of low-grade copper ores.** I. and II. JOSEPH IRVING. *Eng. Mining J.* 113, 714-21, 774-7(1922).—Heap leaching is practiced in Spain and Portugal, South Australia, Arizona, and New Mexico. All classes of Cu ores are amenable. Crushing is not necessary, as pieces of 12-in. size will leach completely. Run-of-mine ore is used, but coarse and fine must be distributed in such a way as to provide for dissemination of air through the heap and insure good percolation. The floor is first prepd. and hardened to prevent seepage loss, often being covered with a layer of slime several inches deep. On this culverts are built of large pieces of ore to assist oxidation and drainage. On this the ore is heaped, up to 60 ft. high. Leaching is partly with fresh H<sub>2</sub>O and partly with spent liquor which has previously gone through the leaching and cementation cycle. If the liquor going on the heap is first passed through a bed of sulfide ore (pyritic filter), its leaching power is much increased and pptn. of Cu from the soln. made easier. The solvent is run first on a portion of the heap for several weeks in such amt. as to dissolve only a small part of the Cu; treatment is then diverted to another part while the first part has a chance to oxidize and heat, the temp. not being allowed to exceed 60°. The next leaching will then complete the soln. of Cu. Treatment of a heap should be complete in 3 to 5 years. Pptn. of the Cu is accomplished by cementation on Fe, either in launders or vats. The latter are better, as large pieces of scrap, such as old converter-shells and furnace-jackets, may be used, while provision for stirring and other mechanical advantages may be introduced. Leaching of ore *in situ* may be practiced in some cases. Details are given of tests, app., and practice at the different localities. A. BUTTS

**Treatment of pyritic concentrates containing tin.** C. W. GUDGEON. *Bull. Inst. Mining Met.* No. 212, 1-8(1922).—The method of concn. of the ore at Mt. Bischoff mill yielded a first product of about 62% Sn and a second one of about 30%. The tails contg. about 0.25% Sn are worked by a special treatment using classifying and concn. to obtain a product of somewhat higher grade with a loss in the tails of only 0.103% Sn. The concentrates thus obtained are roasted; a smelter product consisting of 64 to 68% Sn is made. W. A. MUELLER

**Proposals for testing coke for blast furnace and foundry purposes.** HEINRICH KOPPERS. *Stahl u. Eisen* 42, 569-73(1922).—A coke which has not been heated above 650-800° in its prepn. is more easily combustible and is satisfactory for blast-furnace use. Foundry work requires a heavier coke. The combustibility of a coke can be easily detd. in a small experimental burner. Quant. information can be obtained by heating in an elec. furnace and noting the gas given off at various temps.

R. S. DEAN

**Blast-furnace filling.** D. F. ROBERTS. *J. Iron Steel Inst. (London)* 1922, Adv. proof, 17 pp.; *Engineering* 113, 599-603; *Iron and Coal Trades Rev.* 104, 666-8 (1922).—A general discussion is given of the advantages and disadvantages of the mechanical charging of blast furnaces by the two chief ways, the skip and the bucket methods. The most important question involved is that of good distribution of the charge in the furnace. The various factors that influence this distribution are explained, illustrated, and the reasons stated why, in general, the bucket design is the most favored. The various points are illustrated by drawings of plants in actual operation.

E. F. PERKINS

**The Schürmann furnace.** E. HELLMUND. *Giesserei* Z. 9, 146-51(1922).—A new type of furnace has been devised for reducing both the coke consumption and the S content of the Fe. These reductions are accomplished by preheating the air blast (*German patent* 266,303). Two sep. chambers are constructed on opposite sides of the furnace and the inlet for the air blast has a valve whereby the blast may be shunted through either of these warming chambers. Passing down a previously heated chamber the blast passes through the bottom of the charge and up through the other chamber. When the latter is of sufficiently high temp. the direction of the incoming blast is reversed and the latter thus continuously preheated by this alternation. The blast enters the charge at 800-900° and the exhaust gas is at 100-150°. The coke consumption is reduced to 6.5% (from 8%) and the S content of the Fe 20-30%. The cost of installation of this auxiliary equipment is balanced by the saving in coke with an Fe production of 15 tons per day for 1 yr. Diagrams and illustrations are given. C. C. D.

**The value of clean blast-furnace gas.** N. H. CELLERT. *Mech. Eng.* 44, 305-10 (1922); cf. *C. A.* 15, 3602.—Calcd. savings at 1913 prices from cleaning gas for use in stoves were 16 c. per ton of pig iron, besides the large savings due to longer life of the stoves. Detailed calcs. show that dry cleaning is more economical than wet cleaning. Dry-cleaned gas at 200° in spite of the higher H<sub>2</sub>O content (here 35 grains per cu. ft. against 8) has 6.5% more available heat than wet-cleaned gas at 20°. At \$6 per ton for coke charged this represents a saving of 16 c. per ton of iron in favor of dry cleaning. There is no difference in flame temp. Dry cleaning may also be done at lower cost. Electrical cleaning has possibilities. A. BUTTS

**Desulfurization of cast iron by the Walther process.** MASING. *Naturwissenschaften* 10, 167(1922).—The Walther process has been in operation on a large scale since the first of the yr. It consists in stirring into the molten Fe a desulfuring agent made up of alkali and alk. earth compds.; 40-70% of the total S is thus removed, whereas the Si and C are unchanged. The desulfurization is the more complete the higher the temp. (up to 1450°) and the longer the time (practically 7-15 min.). The reagents added are then removed as slag. The cost of casting by this process is increased approx. 1.5%. This can be easily counterbalanced by the use of cheaper raw material and diminished waste. C. C. DAVIS

**Metallography and physical chemical analyses.** N. S. KURNAKOV. *Messageur sci. tech. russe* Nos. 3, 4, 6(1921); *Rev. metal* 19, 152-3(1922).—A general review of the applications and results of metallography during the past 25 yrs. with special attention to the work in Russia since the establishment of the Russian Metallographic Commission under Tchernov.. W. A. MUDGE

**Physical metallurgy at Columbia University.** E. E. THUM. *Chem. Met. Eng.* 26, 984-7(1922).—A description of the app. and the general methods employed for the teaching of *metallurgy* at Columbia University is given, together with sketches of the app. and pictures of the labs. in use. W. A. MUELLER

**Testing artillery cartridge cases.** J. B. READ AND S. TOUR. *Trans. Am. Inst. Mining Met. Eng.* No. 1151-N, 53 pp.(1922).—Tensile-strength requirements are now sufficiently established by the experience during the war to warrant their being placed in specifications and used in deciding the acceptance or rejection of cases. The  $HgCl_2$  test has been met by reliable mfrs., is a good test for control of the manuf. process, is a sure indication of the behavior of the case in storage, and indicates a metal condition that cannot be detected by chem., physical, or microscopic tests. It should, therefore, be made a definite requirement in the specifications for cartridge cases. Microscopic examn. should be made of a portion of the cases submitted for tensile-strength tests, also of samples of all questionable material. Photomicrographs are essential as a record and for purposes of comparison; their number will depend on conditions. Ballistic tests alone are not a sufficient or proper test of cartridge cases. Except on material that is questionable, metallurgical tests taken with proper dimensions and visual inspection are sufficient and more reliable than ballistic tests. The present requirements and specifications for cartridge-case disks are satisfactory. Indications are that hardness tests, made by the Baby Brinnell machine without cutting up the cartridge case, might be substituted for the tensile-strength test. Such tests would increase the sample, decrease the work, and save the case. The low-temp. anneal (below recrystn. temps.) seems so certain of overcoming all season cracking that its employment in the manuf. of cartridges should be seriously considered. More judgment should be used in rejecting cartridge cases because of slight visual defects. V. O. HOMERBERG

**Engine castings requirements rigid.** H. J. YOUNG. *Foundry* 50, 311-4(1922).—Micrographs show variation in the Fe in the same castings. Heat tends to cause Diesel engine cylinder liners and pistons to grow. Study of requirements is urged. V. O. HOMERBERG

**The phenomena of quenching and their generalizations.** LEON GUILLET. *Rev. metal* 19, 162-77(1922); cf. *C. A.* 15, 3064, 3813.—A continuation of previous work and a general summary. Three types of alloys are discussed: (1) a eutectoid, where there are (a) two solid solns. (Ag-Cu), (b) one solid soln. (brasses, bronzes, Ni-Zn and Al-Fe), and (c) no solid soln. (Fe-C); (2) an alloy having a line of transformation in the solid sepg. a zone of one constituent from a zone of two constituents, where (a) in cooling the path is from a zone of one phase to a zone of two phases (brasses and bronzes) or (b) *vice versa*, (Pb-Sn and Pb-Bi); and (3) an alloy having a zone contg. two constituents sepd. by two irregularly curved lateral lines from two zones of one constituent each (Al-Cu and duralumin). (1) is most important and (3) very interesting since the proportion of both constituents may be changed by the quenching temp.; it is not, however, widely used. The same general laws apply equally well to all cases. The variations in hardness in quenched products, as shown by many Brinnell values, are differences of degree only. Quenching must be done from a point in the  $\gamma$ -range. The brasses always give an austenitic structure, the bronzes and steels are mostly martensitic except where an added element affects the critical point, as in the alloy steels. The effect of Si and Mg individually or simultaneously on the Al-Cu alloys is discussed in detail and many photomicrographs are given to show typical structures. Si and Mg together are necessary to produce the desired properties in duralumin. W. A. MUDGE

**Slip interference theory of hardening.** P. D. MERICA. *Chem. Met. Eng.* 26, 881-4(1922).—Hardness caused by dispersed particles is due to a dislocation in the

spacing of surrounding atoms rather than to intrinsic hardness of the particles themselves. Max. hardness does not involve min. ductility. Extreme cold-work actually causes a slight softening.

V. O. HOMERBERG

**Corrosion of ferrous metals.** R. A. HADFIELD. *Engineering* 113, 419-20(1922).—The prepn. of the various ferrous metals used in the corrosion research of the Institution of Civil Engineers, together with their phys. and mechanical properties, and some general considerations on the subject of corrosion are discussed. V. O. HOMERBERG

**The general effect of electrification on the operation of steel mills.** WILFRED SYKES. *Blast Furnace & Steel Plant* 10, 306-12; *Iron Age* 109, 1557-60(1922). E. J. C.

**Core-oven tests.** F. L. WOLF AND A. A. GRUBB. *Trans. Am. Inst. Mining Met. Eng.* No. 1152-N, 13 pp.(1922); cf. *C. A.* 16, 545.—It is concluded from observations and data that power or fuel costs are decidedly in favor of the oil-fired oven while other considerations such as quality and uniformity of bake, core losses, convenience and cost of tending, cleanliness and noise are decidedly in favor of the elec. ovens.

V. O. HOMERBERG

**Sand problem in a steel foundry.** H. F. CONE. *Iron Age* 109, 985-8(1922).—Mostly mechanical. Machines and methods are described for handling and reconditioning old sand after use in a steel foundry. Plans for a *modern elec. steel foundry* are given.

E. F. PERKINS

**Questions pig iron casting methods.** R. E. NEWCOMB. *Foundry* 50, 316-7 (1922).—The advantages and disadvantages for foundry use of sand-cast pig Fe are compared with those of pig Fe made by the machine casting process.

V. O. H.

**Photomicrographs of steel at high magnification.** R. HADFIELD AND T. G. ELLIOT. *Trans. Faraday Soc.* 16, 156-61(Sept., 1920); *Science Abstracts* 24A, 584.—A review of the early history of photomicrography and a discussion on a number of photographs of steel under various magnifications, the highest of which is 8000 diam., these high magnifications being obtained by means of a 1.5-mm. apochromatic objective and a large camera extension.

H. G.

**X-ray studies on the crystal structure of steel.** ARNE WESTGREN AND GÖSTA PHRAGMÉN. *J. Iron Steel Inst.* (London) Advance proof, 22 pp.(1922); *Engineering* 113, 630-4.—X-ray photograms (according to Debye and Scherrer) of an Fe wire, heated to 800°, 1100° and 1425° have shown that the wire within the so-called  $\beta$ - and  $\delta$ -ranges has a body-centered cubic structure and within the  $\gamma$ -range a face-centered structure. It is thus proved that the transformation that takes place at 900° ( $A_1$ ) is reversed at 1400° ( $A_4$ ). The  $\gamma$ -Fe lattice of austenite steels is enlarged by the dissolved C. A steel with 1.98% C has a somewhat larger lattice when quenched from 1100° than when quenched from 1000°. Also the  $\alpha$ -Fe lattice in martensite seems to be influenced by the C present. The ranges of homogeneous  $\alpha$ -Fe lattice in martensite are extremely small. A steel with 0.80 percent C, quenched in  $H_2O$  from 760°, is on the verge of being totally amorphous. Debye photograms of cementite and of the well known crystal tablets of spiegel Fe are identical. A Laue photograph and investigations of an orientated rotating crystal of the latter type have made it possible to find out the crystal data of cementite. It belongs to the orthorhombic system, its ratio of axis is 0.870: 0.755: 1, and the dimensions of its elementary parallelepiped are 4.53, 5.11, and 6.77 Å. The base group consists of 4 mols.  $Fe_3C$ , which corresponds to a sp. wt. of 7.62

V. O. HOMERBERG

**Influence of dissolved oxides on carburizing and hardening qualities of steel.** E. W. EHN. *J. Iron Steel Inst.* (London) 1922, Advance proof, 39 pp.; *Iron & Coal Trades Rev.* 104, 662-3.—Failure in case-hardening, especially as regards soft spots, is often due to improper steel. Variation of structure of a carburized piece gives a direct indication whether or not the steel is suitable for carburizing. Coarse-grained

structure in case and core of carburized steel with large crystals of pearlite, and clean-cut cementite areas in the hypereutectoid zone, are signs of good or "normal" steel. Curly cementite, disintegration of pearlite in hypereutectoid zone, and fine grain size with rounded pearlite areas in gradation zone and core are signs of an "abnormal" steel. Abnormal steel has a tendency to give a thin case of high C content and to form soft troostitic spots in hardening. Variation in structures obtained with normal and abnormal steel at different carburizing temps. and rate of cooling is shown. Recommendations for carburizing tests on a lab. scale are given. Proof is given that oxides uniformly distributed through the steel are the cause of the different carburizing properties. The ultimate reason is improper deoxidation of the steel when made, and no later treatment can change these properties. The influence of the oxides is explained theoretically. It is shown that the structure of the steel depends on the crystn. during the solidification of the steel in the ingot. A theory of the influence of oxides in hardening is given, founded on the work by Portevin and Garvin. Suggestions for new specifications for steel for ordinary carburizing purposes are given. Heat treatment of all kinds of steel is largely dependent on the presence in the steel of oxides.

V. O. HOMERBERG

**Effect of oxidizing gases at low pressures on heated iron.** H. C. H. CARPENTER and C. F. ELAM. *J. Iron Steel Inst. (London)*, 1922, Advance proof, 7 pp.; *Engineering* 113, 605-6; *Blast Furnace Steel Plant* 10, 317-9.—Samples of Armco, electrolytic, and Swedish Fe were heated from below 900° to above 1000° in an evacuated quartz tube and oxidized slightly without producing any characteristic crystallographic features on the surface of the metal. If, however, a specimen of Cu be introduced as well contg. the gases which are ordinarily present in the metal, a reaction sets in resulting in the gradual production and development of characteristic facets on the surface of the Fe. These are due to the production of what is probably the oxide  $\text{Fe}_3\text{O}_4$ , which subsequently passes to  $\text{Fe}_2\text{O}_3$  without change of form. The oxide of Fe originally produced is isomorphous with  $\alpha\text{Fe}$ , and the orientation of the oxide produced on any given crystal of Fe is detd. by the orientation of the  $\alpha\text{Fe}$  itself. It is, in other words, "a parallel growth" of the  $\text{Fe}_3\text{O}_4$ . Once produced the form of the oxide is uninfluenced by heating the specimen to a temp. at which  $\gamma\text{Fe}$  is formed. A somewhat similar phenomenon was observed 16 years ago by Osmond and Cartaud. The principal agent in the production of the characteristic facets of oxide is the mixt. of gases evolved by the Cu on heating.

V. O. HOMERBERG

**Hydrogen decarburization of carbon steels with considerations on related phenomena.** C. R. AUSTIN. *J. Iron Steel Inst. (London)* 1922, Advance proof, 50 pp.; *Iron & Coal Trades Rev.* 104, 661-2.—An account is given of the influence of time and temp. on the rate of decarburization by H of plain C steels of varying C content, and on the configuration of the recrystallized ferrite grains constituting the decarburized portions. It is shown how the temp. affects the microcharacter of the partially decarburized steels, and detailed descriptions of structures provided by the elimination of C at 680°, at 1000°, and at some "intermediate" temp. are also recorded, while an attempt has been made to indicate diagrammatically how, with a const. time factor, the max. range of any partial decarburization or conversely, the depth from the surface at which no diminution in C content is microstructurally visible, depends on the temp. of experimentation and on the original percentage of C contained in the steel. The effect of time, with a const. temp., on the amt. of decarburization has likewise been graphically depicted, and a comparison drawn between the results obtained and those provided by analogous considerations of the reciprocal process of cementation. A study of the crystal grain structure of the C-free periphery has yielded interesting results, the most striking being the manner in which the initial C content of the steels so profoundly

affects the configuration of the crystal grains comprizing the H decarburized material when the removal of the C is effected at a subeutectoid temp. A theory has been put forward as a possible explanation of the "columnarization" phenomenon observed, and clearly illustrated in the photomicrographs presented. Some exptl. consideration has also been given to the effect of temp. on the rate of diffusion of C or carbide of Fe, in Fe; in all instances the medium employed was a partially decarburized hypereutectoid steel presenting a microstructure consisting of a completely decarburized peripheral zone surrounding an apparently unaltered cone. The results of this phase of the work have been recorded, and discussed in the light of the work of previous investigators, reasons being stated for the conclusion that  $\alpha$ -Fe must have a real soly. for C or carbide of Fe; the degree of soly. depends on the temp., but data have not yet been obtained which admit of a numerical expression for this soly. A figure as a first approximation has, however, been deduced for the diffusion const. or sp. diffusive rate of C in Fe at 650° and at 850°, based on the application of Fick's well known law of diffusion. Decarburization by means of pure dry H has been briefly described, and a comparison made between the observations noted and those previously obtained, under similar conditions, with the moist commercial gas; that the presence of O is not essential for the production of the peculiar "columnar" feature of the crystal grains is demonstrated in this section of the work. Decarburization with a temp. gradient maintained along a steel specimen has incidentally provided 1 or 2 interesting features; the microstructure of a piece of Fe wire which had remained in the furnace during decarburization presented a very interesting appearance and presumably provides an example of decarburization preceded by carburization in the same furnace and under similar conditions. The salient features of the decarburization effected during the maintenance of a temp. gradient have also been recorded.

V. O. HOMERBERG

**Constitutional diagram of the iron-carbon system based on recent investigations.** KOTARO HONDA. *J. Iron Steel Inst.* (London) 1922, Advance proof, 10 pp.—A brief summary of the results of recent investigations of the properties of the alloys of Fe and C and a modified diagram to meet the new requirements are given. The graphitization in Fe-C alloys,  $A_4$  or  $\gamma$ - $\delta$  transformation,  $A_3$  or  $\alpha$ - $\gamma$  transformation,  $A_2$  or magnetic transformation,  $A_1$  or eutectoid transformation, and  $A_0$  or cementite transformation are discussed.

V. O. HOMERBERG

**Stepped  $A_1$  transformation in carbon steel during a rapid cooling.** KOTARO HONDA AND TARIO KIKUTA. *J. Iron Steel Inst.* (London) 1922, Advance proof, 13 pp.—In the rapid cooling of C steel the  $A_1$  transformation takes place at a lower temp. than in slow cooling; the diminution in the temp. increases with the velocity of cooling until it reaches a certain temp., i. e., about 600°. If the velocity of cooling further increases, the transformation point is discontinuously lowered to about 300° or even less. If the velocity of cooling have an intermediate value, the 2 transformations above referred to, usually designated by  $Ar'_1$  and  $Ar''_1$  points, take place during a single cooling. The nature of these 2 transformations was studied in Cr and Ni steels. The transformations were investigated by means of magnetic and dilatometric methods. It is concluded that the  $Ar'_1$  transformation is not a different transformation but merely the retarded  $Ar'_1$  (=  $Ar_1$ ) transformation.

V. O. HOMERBERG

**Delayed crystallization in the carbon steels—formation of pearlite, troostite, and martensite.** A. F. HALLIMOND. *J. Iron Steel Inst.* (London), Advance proof, 1922, 20 pp.—The supersatn. theory is applied to steel. A summary of recent researches on delayed crystn. and inoculation is given, and the origin of pearlite, troostite, and martensite is discussed. The area below the eutectoid point, common to the metastable ranges for cementite and ferrite, is termed the eutectoid area, and indicates those conditions under which the growth of pearlite can occur. The causes that det. the spacing of pearl-



ite are described. Martensite is regarded as a labile shower of  $\alpha$ -ferrite and troostite as a labile shower of cementite; in the latter case the appearance of the cementite is quickly followed by the growth of  $\alpha$ -ferrite due to inoculation by the cementite at a relatively high temp. Also in *Engineering* 113, 767-9(1922).

V. O. HOMERBERG

The formation of globular pearlite. J. H. WHITELEY. *J. Iron Steel Inst.* (London) 1922, Advance proof, 15 pp.—The carbide constituent of pearlite does not at once dissolve completely at  $A_{c1}$ . With coarse-grained hypoeutectoid steel heating for more than 15 min. was needed at  $760^\circ$ ,  $40^\circ$  above  $A_{c1}$ , to effect a complete soln., and much longer periods at lower temps. The persistence of the nuclei also depends to a large extent upon the size of the pearlite grain. Increasing the grain-size retards soln. On cooling, these nuclei, even if ultramicroscopic in size, inoculate the solid soln. at the transition point, and the pearlite so formed is spheroidal and not lamellar in structure. The term "globular" is used to designate this type of pearlite. Globular pearlite can be formed in hypoeutectoid steel at a temp.  $15^\circ$  to  $20^\circ$  higher than lamellar pearlite. To produce the latter a certain degree of supersatn. would seem to be necessary. The formation of globular pearlite from carbide nuclei within the  $\gamma$ -Fe areas offers a method of ascertaining the true equil. point  $A_e$ , since, in slow cooling, as soon as the metastable region is entered, the nuclei initiate crystn. of the carbide and ferrite and lag does not occur. By applying this method to a case-hardened steel contg. 0.52% Mn, the  $A_e$  line in the equil. diagram was found to be horizontal to within  $5^\circ$ . As the temp. falls below  $A_e$ , the rate of formation of globular pearlite is slow at first and then increases rapidly until the point  $A_{r1}$ , at which lamellar pearlite can grow, is reached. The presence of globular pearlite induces an earlier growth of lamellar pearlite in adjoining parts of the solid soln. which may happen to be free from nuclei. In hypereutectoid steels, although the range of temp. above  $A_c$  in which the nuclei persist is wider, globular pearlite is not always produced in cooling. In some steels the tendency for lamellar pearlite to form, notwithstanding the presence of nuclei, is very strong. It is suggested that, in hypoeutectoid steels at any rate, the formation of lamellar pearlite only, during slow cooling, indicates the entire absence of carbide nuclei from the solid soln. Also in *Engineering* 113, 733-6(1922).

V. O. HOMERBERG

Heat of transformation of austenite to martensite and of martensite to pearlite. NOBUO YAMADA. *J. Iron Steel Inst.* (London), 1922, Advance proof, 19 pp.; *Sci. Repts. Tokoku Imp. Univ.* 10, 453-70.—A calorimeter was devised for measuring the heat evolution or absorption at high temps. in the vicinity of  $400^\circ$ . With this calorimeter, the heat of solution of C in Fe was measured by 6 kinds of steel. It linearly increases with the content of C in steels, and amounts to 1300 calories per g. of C. The sum of the heats of transformation  $A_3$ ,  $A_2$ , and of austenite to martensite was measured for 6 kinds of steel by the usual method of mixt. By combining the result of the present expt. with that of Meuthen, the heat of the allotropic transformation austenite to martensite was obtained. It linearly increases with C and amounts to 5.6 calories per g. for eutectoid steel. The sp. heats of troostite, sorbite, and pearlite have the same value within the limit of exptl. error. The results of the present investigation confirm the correctness of Professor Honda's theory of the  $A_1$  transformation.

V. O. HOMERBERG

Inner structure of the pearlite grain. N. T. BELAIEV. *J. Iron. Steel Inst.* (London) Advanced proof, 1922 27 pp.; *Engineering* 113, 634-8.—The arrangement of cementite lamellae in a pearlite grain is roughly parallel one to another and to the crystallographic plane of the grain, presumably to 1 face of the cube. A secant plane perpendicular to that face will be normal to the lamellae; the angle of inclination  $\omega$  for that plane will be zero. All the ( $N$ ) lamellae of the grain will be seen on the normal plane. The distance between 2 lamellae ( $\Delta$ ) on such a plane will be the actual distance, and is called  $\Delta_p$ . As the angle  $\omega$  increases, the number ( $n$ ) of lamellae seen on a section of the same grain

decreases and the apparent distance between 2 lamellae  $\Delta_\omega$  increases. As  $\cos \omega = n/N = \Delta_0/\Delta_\omega$  the graph of natural cosines will show the ratio of decrease in the number of lamellae and of the increase in the distance between the lamellae or the coarseness of the structure of the grain. The angle  $\omega$  may be computed from  $\cos \omega = \Delta_0/\Delta_\omega$ , where the values of  $\Delta_0$  and  $\Delta_\omega$  are obtained by direct measurement on a suitable photomicrograph. In that way the angle of inclination of pearlite grains may be computed with a sufficient accuracy. When the angle  $\omega$  approaches  $80^\circ$  then the distance  $\Delta_\omega$  becomes 5 times greater than  $\Delta_0$ , 10° times at  $84^\circ$ , and  $20^\circ$  at  $87^\circ$ . The aspect of pearlite, as we are accustomed to see it, must exhibit a considerable change on such sections. Examn. of sections of prepd. alloys confirm these conclusions and prove that the pearlite grains in hypoeutectoid steel, eutectoid steel, and hypereutectoid show on a section a change in coarseness and character of structure as expected from the equation  $\cos \omega = \Delta_0/\Delta_\omega$ . The value of  $\Delta_0$  becomes, therefore, of importance for every pearlite steel, and may be taken as a measure of the thermal conditions during the  $Ar_1$  transformation. A direct way of measuring  $\Delta_0$  for values not under  $0.25\mu$  is given, and another method, based on the formula  $\Delta_0 = \Delta_\omega \cos \omega$  or  $= \Delta_\omega / \sec \omega$ , is recommended for smaller values.  $\Delta_0$  may be taken as one of the characteristics of steels, and values of  $\delta_0$  may be computed to det. various kinds of pearlite and sorbite pearlite. The following values for  $\Delta_0$  are obtained by direct method:  $\Delta_0 = 1.25\mu$  (hypereutectoid),  $0.35\mu$  (hypoeutectoid steel),  $0.30\mu$  (eutectoid steel). As the pearlite of the hypereutectoid steel is exceptionally coarse the 2 last figures are taken as being fairly close to the usual values of  $\Delta_0$  met with in practice. The micromillimeters then will read:  $\Delta_0 = 350\mu\mu$  (hypoeutectoid),  $300\mu\mu$  (eutectoid steel). By the indirect method the  $\Delta_0$  is detd. for one of Sir Robert Hadfield's steels. For that steel  $\Delta_0(H) = 100\mu\mu$ . As the diameter of a cementite ( $d_c$ ) lamella may be taken as  $1/3$ , or better  $1/4$ , of the total distance between the lamellae  $d_c = \Delta_0/4$ , the following values were obtained:  $d_c$  (hypoeutectoid)  $= 90\mu\mu$ ,  $d_c$  (eutectoid)  $= 75\mu\mu$ ,  $d_c(H) = 25\mu\mu$ . Assuming that the diam. of the grain  $D = 100 \Delta_0$ , the cementite lamellae are represented as films and a suggestion is made as to the interior structure of the pearlite grain.

V. O. HOMERBERG

The resistance of steels to torsion or bending between ordinary temperatures and the visible red range. J. SEIGLE. *Rev. metal.* 19, 178-80 (1922).—When the torsional strength of a mild or a hard steel bar was detd. while a portion for the bar was heated, the following facts were noted: (1) Practically all twisting occurred in the heated portion; (2) at the yellow heat ( $250^\circ$ ) the torsional strength increased 30-45%, (3) at the blue ( $340^\circ$ ) it was 20-25% less than that of the original bar, and (4) at the visible red ( $600-700^\circ$ ) it was only about  $1/4$  as great as in the original steel.

W. A. MUDGE

Use of the contact electromotive force for identifying various steels. GALIBOURG. *Compt. rend.* 174, 547-50; *Iron Age* 109, 1291-2 (1922).—The Brinell hardness detn. upon a remelted steel permits its identification with reasonable accuracy. For special steels this does not hold, as they differ widely in hardness according to their compn. For testing these steels the method described answers very well. A Hg bath is heated to  $120^\circ$  by means of a nichrome resistance heating unit. A wire of electrolytic Fe dips into the bath and is attached to one terminal of a millivoltmeter. The other terminal is connected with a hollow metallic clamp which is cooled by circulation of water and which holds the sample to be tested. This piece, held by one end in the clamp, is brought into contact at its other end with the bath. After 4-5 sec. the pointer of the millivoltmeter stabilizes. The only function of the Hg is to close the circuit with a perfect elec. and thermal connection between the standard Fe wire and the piece to be tested. Several curves show the e. m. f. of different carbon and special steels at  $120^\circ$ ,  $200^\circ$ , and  $300^\circ$ . For the higher temps. a bath of Pb is employed. Temper has little effect upon the

appearance of the curve traced by a certain steel, thus dispensing with the necessity of giving a special treatment to pieces kept for examn. The differences in e. m. f. produced by different steels are sufficient to permit classification of ordinary and special steels after testing at the one temp., 120 deg., in a somewhat different order than that detd. by the Brinell hardness. This in consequence furnishes a second equation, the first being given by the hardness, for presuming the nature of a steel which cannot be analyzed conveniently.

J. T. R. ANDREWS

**Magnetic researches on nitrogenized steels.** KIVOSHI KIDO. *Sci. Repts. Tohoku Imp. Univ.* 10, 471-78(1921).—The object of the paper is to ascertain in what form the nitrides of iron occur in steel. The method of magnetic analysis explained in detail in *Sci. Repts. Tohoku Imp. Univ.* 5, 285(1916) was used. Four forms of magnetization-temp. curves were obtained. These curves have transformations at (1) 215° and 750°; (2) 470°, 620°, and 750°; (3) 250°, 470°, and 620°; (4) 350°, 470°, and 620°. On a plot with N content as abscissa and C content as ordinates, 4 distinct fields are obtained, each having the above transformation points. The following compds. at the above transformation points were definitely located; Fe<sub>3</sub>C at 215°, Fe<sub>3</sub>N at 250°, double carbide  $\alpha$  at 350°, Fe<sub>2</sub>N at 470°, and double carbide  $\beta$  at 620°. These expts. resulted in the discovery of the two new double carbides of Fe and N.

E. F. PERKINS

**Selection and heat treatment of tool steel.** S. C. SPAULDING. *Blast Furnace Steel Plant* 10, 224-7(1922).—The detg. points of the adaptability of steel for the making of tools are capability of fabricating, machining, forging, pressing, etc., and possibility of safely hardening or suitably heat treating to put in condition for use. These points are discussed with special reference to the selection of the proper steel.

V. O. HOMERBERG

**Steel wire and wire drawing.** H. A. ATKINS. *Engineering* 109, 731-4, 749-52 (1920).—The theory and practice of wire drawing are described. Photomicrographs show the structure of the material before, during, and after drawing. A tensile-strength curve is shown for a wire of 0.80 C steel. The wire rod has a tensile strength of 58 tons to the sq. in. It is retempered twice in drawing down to 30 gage; this increases the tensile strength to 210 tons per sq. in. The patenting process consists in running the wire continuously through a tube furnace and cooling it in the air or some other medium, with the object of regulating the rate of cooling to give a structure with the desired strength and toughness. The effect of impurities in steel on wire-drawing is considered.

V. O. HOMERBERG

**Steel for forge welding.** F. N. SPELLER. *Blast Furnace and Steel Plant* 10, 259-61; *Raw Material* 5, 164-5(1922).—The principal factors (method of manuf., chem. compn., fluxing quality, susceptibility to heat and welding temp.) affecting the welding quality of steel are discussed and the av. results of 80 tests made on forge welds of hammer-welded pipe are compared with the original material. Tests have demonstrated that both steel not over 0.15% C and min. tensile strength of 47,000 lb. per sq. in. and that not over 0.20% C and min. tensile strength of 52,000 lb. per sq. in., are satisfactory for forge welding of pipe lines, penstocks, tank-car work and similar construction. The most important consideration to produce uniformly good results in the forge welding of steel is suitable material, well trained operators and adequate facilities for the control of operations.

V. O. HOMERBERG

**Many factors control iron quality.** J. E. FLETCHER. *Foundry* 50, 352-5(1922).—Melting conditions both in the blast furnace and in the cupola have effects on the metal not always indicated by the usual chem. analyses.

V. O. HOMERBERG

**Manufacture of high-speed and tungsten steels.** K. DARVES. *Chem. Met. Eng.* 26, 869(1922).—Carbides in high-speed steels are not made sol. by any heat-treatment. They form a eutectic, which melts at relatively low temps. The m. p. of this eutectic

in Cr steels lies at about  $1,150^{\circ}$  and in W steels as low as about  $1,060^{\circ}$ . A ternary eutectic exists in high-speed steels contg. Cr and W, and it is evident that the eutectic is melted after a careless high heat and squeezed out by subsequent forging.

V. O. HOMERBERG

**Damascene steel.** MASING. *Naturwissenschaften* 10, 166(1922).—Emphasis is laid on the little known high degree of hardness and tenacity of Damascene steel contg. 1.5% C (cf. *C. A.* 15, 3968).

C. C. DAVIS

**Failure of cast and high-silicon iron in fuming sulfuric acid.** T. F. BANIGAN. *J. Ind. Eng. Chem.* 14, 323(1922).—Expts. on metallic Si and Si-Fe alloys indicate that the failure of cast Fe and malleable castings in fuming  $H_2SO_4$  is due to oxidation of the particles of Si in the casting to particles or crystals of  $SiO_2$ , which, being larger in vol. than the original Si particles, produce internal strain. Cast Fe, with as low Si content as ordinary steel, should be as satisfactory as the latter for use with fuming  $H_2SO_4$ , and any reduction in Si content should improve it for this use.

V. O. H.

**The rate of combination of copper and phosphorus at various temperatures.** C. A. EDWARDS AND A. J. MURPHY. *Engineering* 113, 697-700(1922).—See *C. A.* 16, 1928.

E. H.

**Making hot-pressed or forged brass.** L. S. LOVE. *Iron Age* 109, 1581-3(1922).

E. J. C.

**Duralumin, its properties and commercial possibilities.** W. B. SROUT. *Brass World* 18, 129-30(1922).

C. G. F.

**Monel metal, a natural non-ferrous alloy.** M. A. HALL. *Brass World* 18, 107-11(1922).—Discussion of melting the alloy in an oil-fired and in a Snyder furnace. The Snyder handles 1000 lb. per heat; the roof was built of ganister and silica brick; after superheating to  $1550^{\circ}$ , the metal is deoxidized with a green pole, as in Cu practice; poling continues for about 3 min. then the Snyder is closed again and the arc played for a short time; the melt is sampled and if the report is satisfactory the metal is run into medium-sized bull ladles and about 0.1% of Mg metal added as a deoxidizer. Monel is difficult to keep fluid so as to run easily. It shrinks twice as much as cast Fe. Lumberton and Albany sands give good results; they must be coarse to allow the escape of large vol. of gas. Details on annealing, pickling and forging are included.

C. G. F.

**Metallurgical improvements in the Springfield rifle.** J. S. HATCHER. *Army Ordnance* 2, 351-3(1922).

E. J. C.

**The non-ferrous metal industry. Aluminium; zinc.** A. L. SCOTT. *Brass World* 18, 121-4(1922).—S. discusses methods of casting, rolling, properties, etc.

C. G. F.

**The welding of castings.** G. MARDUS. *Giesserei Z.* 9, 94-8(1922).—A questionnaire is published for foundries in an attempt to obtain all possible information concerning the best methods and the difficulties of the thermite, autogenous, H-O, elec. and liquid-Fe methods of welding.

C. C. DAVIS

**DUPONCHELLE, J.:** *Comment on pratique la fonderie.* Paris: Dunod. 486 pp. 52 fr. Reviewed in *L'Age de fer* 37, 956(1921).

**Metal Statistics for 1922.** New York: American Metal Market & Daily Iron & Steel Rept. 512 pp. \$1. Reviewed in *Metal Ind.* 20, 191(1922).

**RUSE, RUDOLF:** *Metallographie in elementarer Darstellung.* 2nd Ed. Leipzig: Leopold Voss.

**Mineral flotation.** R. E. SAYRE. U. S. 1,415,899, May 16. A flotation mixt. is formed of acetone condensation products or other solvent having frothing properties together with thiourea compds.

**Ore-flotation apparatus.** H. C. and E. A. COLBURN. U. S. 1,415,314, May 9.

**Ore-flotation apparatus.** D. D. MOFFAT. U. S. 1,415,105, May 9.

**Concentrating ores.** A. E. ALEXANDER. Brit. 173,830, Sept. 13, 1920. Pitch obtained from resin, particularly that obtained by the destructive distn. of resin or of wood-tar, is utilized as a frothing agt. in the concn. of ores by flotation. The pitch is dissolved in a soln. of NaOH or potash,  $\text{Na}_2\text{CO}_3$  or  $\text{Na}_2\text{HCO}_3$ , potash, or  $\text{NH}_3$ ,  $\text{NH}_4$  salts, phosphates of Na or K, or in  $\text{CS}_2$ , alc., or acetone, or in combinations of these, and such soln. may be used alone as the frothing agent or in combination with other agents such as coal tar, creosote, water-gas tar, Na oleate, etc. An oxidizing agent such as  $\text{H}_2\text{O}_2$  or  $\text{KMnO}_4$ , or other materials such as Na silicate, alum, or a weak acid such as boric acid, may be present in some cases.

**Dehydrating ore slimes.** M. A. PARMETER. U. S. 1,415,387, May 9. Slimes such as those from mining operations are dehydrated by mixing them with 1% of finely powd. rosin and filtering.

**Treating sulfide ores.** C. J. REED. U. S. 1,415,897, May 16. Sulfide ores such as those of Fe are heated under non-oxidizing conditions to vaporize S, the residue is treated with  $\text{H}_2\text{SO}_4$  to evolve  $\text{H}_2\text{S}$  and the metal sulfate formed is then converted into oxide and  $\text{SO}_2$ .

**Treating lead-zinc sulfide ores.** N. C. CHRISTENSEN. U. S. 1,415,796, May 9. Ore or concentrate contg. sulfides of Pb and Zn is treated with hot concd.  $\text{H}_2\text{SO}_4$ , the hot acid soln. is sepd. and cooled to effect pptn. of  $\text{ZnSO}_4$ . The residue of ore or concentrate is treated with a hot concd. soln. of HCl or  $\text{FeCl}_3$  to dissolve Pb and Ag as chlorides and the Pb and Ag are recovered from this soln. after its sepn. U. S. 1,415,797 relates to extn. of Zn in dil.  $\text{H}_2\text{SO}_4$  soln. and then concg. the soln. to cause pptn. of  $\text{ZnSO}_4$ .

**Zinc ore briquet.** D. B. JONES. U. S. 1,415,094, May 9. Zn ore is briquetted with a reducing agent such as coal, NaCl, fireclay and bauxite, preparatory to smelting to vaporize Zn.

**Treating chromium ores.** W. H. DYSON and L. AITCHISON. Brit. 176,729, Oct. 28, 1920. Ores contg. oxides of Cr are treated for the purification or concn. of the Cr constituent by submitting the ore to the action of a halogen or gaseous halogen acid, *e. g.*, Cl or HCl, or a mixt. thereof, with or without the addn. of H, at such a temp. as to convert some of the constituents of the ore into volatile halogen derivs. The temp. or the nature of the halogen atm. may be adjusted or varied so as to obtain selective distn. of the halogen derivs.; or two or more derivs. may be volatilized and collected together, or separately collected by fractional condensation or by absorption in a solvent for one or more of the constituents. *E. g.*, the Fe may be volatilized from crushed and washed chromite by treatment at about  $900^\circ$  with a mixt. of HCl and H, the Cr being afterwards volatilized by raising the temp. to  $1200^\circ$  and passing Cl over the residue; or the Fe and Cr may be volatilized together by heating throughout at  $1200^\circ$ .

**Smelting copper ores.** P. P. BUTLER and H. H. SROUT. U. S. 1,416,262, May 16. Cu-bearing slag is fused with a washing ore and superheated in a reverberatory furnace to produce a low-Cu high-Fe mat, which settles out.

**Treating tungsten ores.** W. H. DYSON and L. AITCHISON. Brit. 176,428, Oct. 28, 1920. Ores contg. oxides of W, *e. g.*, wolframite or scheelite, are treated for the purification or concn. of the W constituent by submitting the ore to the action of a halogen or gaseous halogen acid, *e. g.*, Cl and HCl, or a mixt. thereof, with or without the addn. of H, at such a temp. as to convert some of the constituents of the ore into volatile halogen derivs. The temp. or the nature of the halogen atm. may be adjusted or varied so as to obtain selective distn. of the halogen derivs.; or two or more derivs. may be volatilized and collected together, or separately collected by fractional condensation or by absorption in a solvent for one or more of the constituents. *E. g.*, the Sn may be volatilized

from crushed and washed wolframite by treatment at about 600° with a mixt. of Cl and HCl; the W, Fe, and Mn may be thereafter volatilized by raising the temp. to 1000°, and collecting the vapors in H<sub>2</sub>O or dil. acid, whereby the Fe and Mn are obtained in soln. while the W is pptd., such ppt. being washed and ignited to obtain tungstic oxide.

**Treating vanadium ores.** A. GILDEMEISTER. U. S. 1,415,028, May 9. Ores contg. V<sub>2</sub>O<sub>5</sub> are treated with dry Cl in the presence of a reducing agent such as C or CO at a temp. above the b. p. of vanadyl trichloride but not above about 400° to distil off the trichloride formed.

**Treatment of iron sand or powdered iron ores.** YÔ NAITO. Jap. 39,261, July 14, 1921. A mixt. of 2 parts of iron sand and 1 part of powdered coal is heated in the absence of air at about 1,000° to form coke contg. Fe. This is piled in the air and treated with SO<sub>2</sub>, Cl, caustic alkali soln., or sea water, by which Fe is changed mainly to hydroxide. The product is used for manuf. of pig Fe in a smelting furnace without additional coke.

**Rotary kiln and smelting furnace for smelting iron ores.** J. LUND. U. S. 1,415,183, May 9.

**Separation of copper from other metals.** MASAO UCHINO, NAGAO TAKATSU, and FURUKAWA KÔGÛ KÂSUHIKI KAISHA. Jap. 39,184, July 8, 1921. A mixt. of metallic oxides, composed mainly of CuO, is dissolved in H<sub>2</sub>SO<sub>4</sub> and a sol. chloride, such as NaCl is added. Cu<sub>2</sub>Cl<sub>2</sub> is pptd. By adding Fe to the filtrate metallic Cu seps. out. By boiling Al, Zn, etc. are pptd. from the filtrate as neutral sulfites. Recovery of Cu is 99.9% and that of *aluminium* 70–99.9%.

**Copper from sulfate solutions.** H. M. WILCOX. U. S. 1,416,147, May 16. Spent liquor is continuously withdrawn from the top of a ppgt. tank or boiler and additional CuSO<sub>4</sub> soln. is introduced at the bottom in proportionate amt. Pptd. Cu is removed from the bottom of the tank by a conveying device without emptying the entire tank contents.

**Reducing tungsten or similar metals.** A. BRIDGE. U. S. 1,415,518, May 9. A thermic mixt. such as oxide of Mo, Ta, Ti, W, V, or Zr and Al, Mg or Ca is placed with in a surrounding insulating mass which may be formed of Al<sub>2</sub>O<sub>3</sub>, CaO and MgO, all contained within a closed air-tight casing resistant to high pressure, and the thermic mixt. is electrically ignited to effect reduction.

**Refining of molybdenum.** YASUMORI MOCHIDA. Jap. 39,167, July 7, 1921. Addition to 34,818. Molybdenite is heated to redness for 30 min. in a shallow pan; P or S in the ore is expelled and black scales of slightly oxidized MoS are formed. Ten parts of the product are mixed thoroughly with 3 of powdered Al and 1 of powdered Mg and burned. Freed Mo is absorbed in the excess of Al and sepd. from the slag.

**Granulating molten slag by water treatment.** W. SCHUMACHER. U. S. 1,416,069, May 16.

**Steel manufacture.** J. C. M. KUBASTA. Brit. 176,576, Jan. 10, 1921. In heat-treating steel, the formation of a soft skin due to decarburization of the surface layer is prevented by carrying out the heating-process in the presence of oxidizing gases, preferably O, in sufficient quantity so that not only is the C removed but the Fe in the surface layer is converted into FeO or Fe<sub>2</sub>O<sub>3</sub> so that the new metallic surface is of normal C content. The steel is heated in a soft-iron vessel and when the first crit. point is reached, O is supplied. After the treatment is completed, the supply is continued to flush out the gases liberated and then stopped. The O remaining is consumed by conversion of the FeO produced into Fe<sub>2</sub>O<sub>3</sub> and thereby air is drawn into the heating-vessel, the O of the air being similarly consumed leaving an inert N atm. in which the cooling is completed.

**Steel.** H. G. C. FAIRWEATHER. Brit. 176,610, Jan. 31, 1921. Si-Mn-Cr steel

low in C is made by prepg. a bath of steel of the required C content preferably in a Martin furnace and adding thereto in the furnace, immediately before tapping, the required amt. of ferro-Mn. The ferro-Si and ferro-chrome, preferably previously melted together in an elec. furnace, are thereafter added to the steel in the ladle.

**Alloy for chemical apparatus.** F. A. FAHRENWALD. U. S. 1,415,233, May 9. Pd 10-40 and Au 90-60% form an alloy which is adapted for use as a substitute for Pt and Pt alloys in making chem. ware, elec. app. or in dentistry.

**Alloy steel tools.** A. BORRER. U. S. 1,415,085, May 9. Tools for high-speed work are formed by direct casting of alloy steel which may contain V, Cr, W and Mn and which is free from internal marks and of uniform internal structure.

**"Metal-scavenging alloy,"** H. G. C. THOFERN. U. S. 1,415,733, May 9. A U-Al alloy adapted for use in purifying Al alloys or other metals is prepd. by melting together ferro-U and Al and allowing the alloy to cool after sepn. from slag.

**Alloy for electrical heating elements.** P. A. E. ARMSTRONG. U. S. 1,416,436, May 16. An Fe alloy contg. Cr about 14% and C 0.1-0.6%.

**Case-hardening metal articles.** G. C. NIXON and F. C. RAAB. U. S. 1,415,260-1, May 9. Cam shafts, gears or other articles to be hardened are covered with an adhering carburizing mixt. such as tar and granular carburizing substances and heated.

**Rotary muffle furnace.** J. R. C. AUGUST. U. S. 1,415,424, May 9. The furnace is electrically heated and is adapted for case-hardening metal articles.

**Carburizing metals.** N. D. NIELSEN. U. S. 1,416,501, May 16. Pulverized dried whole fish bodies are used as carburizing material. Cf. C. A. 16, 1207.

**Anti-rust compositions.** J. BRAUMONT. Brit. 176,246, Feb. 25, 1921. A rust-preventing compn. for the protection of bright metals is made by mixing lard, black lead, and camphor. The approx. proportions by wt. are 16 pts. of lard, 4 pts. of black lead, and 1 pt. of camphor.

**Prevention of erosion of rubber-insulated tin-plated copper wire.** TÔICHIRO ASANO, MINORU ÔSUMI, and KABUSHIKI KAISHA SUMITOMO DENSEN SEIZOJO (Sumitomo Electric Wire Works). Jap. 39,151, July 6, 1921. To prevent the erosion of Sn-plated Cu wire covered with rubber, the wire is previously treated with aq. or alc. soln. of Cd(AcO)<sub>2</sub> or other salts of Cd or Zn. It is then covered with raw rubber and vulcanized as usual. Formation of SnS or CuS is prevented and CdS or ZnS formed in vulcanization does not attack rubber.

**Bronze.** MINORU AKITA. Jap. 39,233, July 30, 1921. A bronze of Cu 75-80, Al 7.5-11, Ni 4-6, Zn 0.5-2, Fe 2-5, P 0.1-0.5, and Mg 0.1-0.5%. It is equivalent to steel in the tensile strength and hardness, resistant to acids, sea and mineral waters, and is easily subjected to mechanical treatment.

**Soldering or welding aluminium.** P. DE CLAMECY. U. S. 1,415,925, May 16. A soldering compn. is formed of Al 180, Sn 18, AgNO<sub>3</sub> 1 and AgCl 1 pt.

## 10—ORGANIC CHEMISTRY

CHARLES A. ROULLER

Dr. h. c. Traugott Sandmeyer. ALFR. CONZETTI. *Schweiz. Chem. Ztg.* 1922, 279-81.—An obituary. E. J. C.

A domestic synthetic camphor industry. ANON. *Chem. Age* (N. Y.) 30, 211-2 (1922). E. J. C.

Development of organic chemistry up to 1800. E. P. HÄUSSLER. *Schweiz. Apoth. Ztg.* 60, 102-8, 157-62, 221-6 (1922).—Various causes, e. g., the notions of alchemy, its leaning to metals and high temps., delayed development of theoretical org. chemistry. The history of the manuf. of org. chemicals, e. g., starch, cream of tartar, indigo, cane sugar, milk sugar, HKC<sub>4</sub>O<sub>4</sub>, Rochelle salt, etc., and the ancient processes of dyeing,

fermentation, etc. show a practical knowledge of org. chemistry previous to Scheele's time. Much literature is quoted.

S. WALDBOTT

**Composition of paraffin wax. I. Action of air and oxygen on paraffin wax.** FRANCIS FRANCIS. *J. Chem. Soc.* 121, 496-500(1922).—Paraffin wax, m. 55-6°, was not attacked by the rapid passage of air for 280 hrs. at 110°, nor by O for 700 hrs. at 100°. After 1276 hrs., O at 100° gave a product containing 74.7% C, 11.6% H and 13.7% O. **II. Action of air and oxygen on paraffin wax containing turpentine.** *Ibid* 500-2.—On adding 5% of turpentine to the wax and passing air for 333 hrs. at 101-3°, the product contained 10.8% O, and O in 696 hrs. at 100° gave a product with 19% O, which was the same after 936 hrs. The m. p. of the product fell to 34-40° after 600 hrs. when the O content was 15%, but rose to 39-43° after 936 hrs. Moisture inhibits oxidation if the reaction has not begun, but has no effect if oxidation has started. Synthetic dotriacontane and hexadecane were not oxidized. **III. Minor products of the oxidation, and the action of turpentine.** *Ibid* 502-3.—H<sub>2</sub>O, CO<sub>2</sub>, and HCO<sub>2</sub>H are formed, in part by the oxidation of the turpentine. About 40% of the latter was carried over unchanged by the air current, also 45% of oxidized turpentine, and a small amt. of liquid acids, called provisionally "γ-acids." **IV. Investigation of the products of air oxidation.** *Ibid* 503-5.—In addition to the volatile products already named, the reaction flask contained about 3% of γ-acids, of low mol. wt., 59% of acidic substances with mol. wts. corresponding to that of the paraffin used, and 39% of non-acid oxidized wax containing some unchanged hydrocarbons. The oxidized paraffin resembled beeswax, and was sepd. by dissolving 1:4 in hot abs. EtOH, adding 40% NaOH, and pouring the soln. into hot H<sub>2</sub>O. On cooling, the upper layer consisted of wax and inert oxidized material, while the lower was a soln. of Na salts, which on acidifying gave a dark oil which solidified when cool. The sepn. is not sharp. The soln. after acidifying contained small amts. of sol. acids, which were the same as the material carried over by the air, and contained 59.86% C, 8.44% H, and 31.70% O, mol. wt. in boiling Me<sub>2</sub>CO 202, acid value 309. **V. Investigation of acidic substances from air oxidation.** (With JOHN C. POPE) *Ibid* 506-7.—By dissolving the mixt. of inert and acidic substances in alk. 50% EtOH and extg. with petr. ether, the inert material can be removed, and the Na salts converted into Ba salts, which were also extd. with petr. ether, giving sol. Ba salts (A), and insol. Ba salts (B). The acids from A were termed "α-acids," liquid, mol. wt. 452, acid value 141, C 72.1%, H 11.2%, O 16.7%. The acids from B were termed "β-acids," m. 43.5°, mol. wt. 326, C 73.0%, H 12.1%, O 14.9%. **VI. Non-acidic substances from air oxidation.** *Ibid* 507-9.—These contain 5-6% of O, and are very difficult to sep. from unchanged paraffin by vacuum distn., but most of the hydrocarbons cryst. from the soln. in boiling Me<sub>2</sub>CO, giving an impure oxidized material with 7.8% of O. The purest material was obtained from the petr. ether used in extg. the Ba salts (see V), or during sepn. of Pb salts, and was liquid, containing about 75% C, 12% H and 13% O. About 1.5% of a substance practically insol. in Me<sub>2</sub>CO was found, with a very high mol. wt. The α- and β-acids together make up about 32% of the total material, the γ-acids 2.5%, inert oxidized hydrocarbons 10%, hydrocarbons m. 55-64°, 19%, hydrocarbons with non-acid material containing 3-4% O, 16%, and a similar mixt. with 7-8% O, 17%. **VII. Separation of products of oxidation with oxygen in the presence of turpentine.** *Ibid* 509-10.—O at 100° causes more profound oxidation, giving 47% of β-acids, 7% of liquid γ-acids, 14% of liquid δ-acids containing 54.6% C, 7.8% H, and 37.6% O, with 25% of non-acid material, of which 15% was unchanged hydrocarbons. **VIII. Products of oxidation with oxygen in the absence of turpentine.** *Ibid* 510.—At 100° oxidation sets in rapidly after 700 hrs., giving 38% of β-acids, 8% of liquid γ-acids, and 9% of δ-acids, as well as 42% of non-acid material with only 3.3% O, showing a high content of unchanged hydrocarbons. **IX. Classification of acids formed in oxidation processes.** *Ibid* 511.—The 4 classes of acids, α, β, γ, and δ, not having been obtained pure, no formulas are given. The



$\alpha$ - and  $\beta$ -acids are the chief products of air oxidation, mean analysis 73.3% C, 11.4% H, and 15.2% O, with little variation, insol. in  $H_2O$  or dil. EtOH, mean mol. wt. 408. Oxidation with O gives chiefly solid  $\beta$ - and liquid  $\gamma$ -acids. The  $\delta$ -acids are somewhat sol. in  $H_2O$ , but have not been further investigated. By means of Pb salts, the  $\alpha$ -acids have been purified to some extent, and the  $\beta$ -acids sepd. into at least 4 constituents. X. Nature of unoxidized hydrocarbons. (With REGINALD H. COYSH). *Ibid* 511-3. —Inert material which had been twice oxidized was dissolved in  $Me_2CO$ , and the sepd. hydrocarbon distd. at 0.5 mm. and oxidized in the presence of 5% of turpentine with O at  $100^\circ$ . After 672 hrs. 6.4% of O was present, whereas the original paraffin wax would have contained about 18% O after this time. The fresh wax was therefore fractionated at 0.5 mm. The fraction b.  $170-80^\circ$  and also that b.  $>232^\circ$ , when treated with O in the presence of turpentine at  $100^\circ$ , took up only 3-4.5% of O, while the fraction b.  $190-200^\circ$  showed 15% O after oxidation, and the fraction b.  $205-20^\circ$  took up 12% O. Work is now being continued on the portion b.  $190-220^\circ$ , which apparently contains the most oxidizable constituents of the wax. M. R. SCHMIDT

Acetylene condensations. I. Attempts to determine the constitution of cuprens. H. P. KAUFFMANN AND M. SCHNEIDER. *Ber.* 55B, 267-82(1922); cf. C. A. 13, 1825.—Comparative expts. with reduced Cu, CuO,  $Cu_2O$  and  $Cu_2Fe(CN)_4$  (previously heated 15 min. in a current of air at  $250^\circ$ ) showed that the last gives the best yields of cuprene (A) (8 g. from 0.8 g. of the catalyst heated 4 hrs. at  $240-50^\circ$  in perfectly pure  $C_2H_2$ ). The condensation product varies in color with the catalyst and the length of the heating; that obtained with  $CuFe(CN)_4$  is yellow to light brown; if the length of heating is short the mass consists of loose, voluminous, very light flocks whereas if the heating has been continued 6-8 hrs. the product is a cork-like solid. Numerous analyses on products prepd. at different temps. and with different catalysts confirmed Gooch and Baldwin's conclusions (*Z. anorg. chem.* 22, 236(1900)) that A is not homogeneous; the compn. of the products varied between  $(C_{11}H_{10})_x$  and  $(C_{13}H_{10})_x$ . The Cu can be removed with boiling HCl only with very great difficulty; even after 8 hrs. boiling with 20% HCl the Cu content decreased only from 7.06 to 2.21%; only after several hrs.' boiling with *aqua regia* could a product with negligible Cu content be obtained. The most concd.  $HNO_3$  carbonizes A but 50%  $HNO_3$  gives with A prepd. with  $Cu_2Fe(CN)_4$  a clear yellow soln. which on evapn. and neutralization with  $NH_4OH$  yields  $NH_4$  mellitate; if, instead of neutralizing with  $NH_4OH$ , the soln. is highly dild. with  $H_2O$  there is formed a brown mellogen-like ppt., which on further treatment with 80%  $HNO_3$  likewise gives mellitic acid and yields  $BzOH$  on dry distn.; the  $HNO_3$  mother liquor from the original brown ppt. gives on neutralization with  $Ba(OH)_2$  a mixt. of Ba salts, from which  $C_{10}H_8$  is obtained on dry distn. A is exceedingly inert towards halogens; only by using  $FeCl_3$  or  $FeBr_3$  as catalyst was it possible to obtain a Br deriv. sol. in org. solvents. Br in  $H_2O$  or org. solvents does not attack A, while liquid Br alone carbonizes it. The best results were obtained by heating a thin paste of A with  $H_2O$  and Br and a little  $FeBr_3$  in a sealed tube at  $100-30^\circ$ . A product so obtained, sol. in alc. and  $Et_2O$ , had the compn.  $C_{14}H_{10}Br_6$  and gave mellitic acid with  $HNO_3$  in sealed tubes; it is possibly a hexabromohexahydro-triphenylene; attempts to prep. the corresponding hydrocarbon by removing the Br failed, as the substance immediately condenses to an A-like product when the Br is removed. A is considered to be a hydrocarbon with proportionately less H than  $C_2H_2$  and resembling the natural coals in its properties. C. A. R.

Exchange of the halogen in unsaturated aliphatic halogenated hydrocarbons. I. H. P. KAUFFMANN. *Ber.* 55B, 249-60(1922).—While the halogen in monohalogenated aliphatic hydrocarbons is easily replaceable, a more or less marked sluggishness in reactivity manifests itself when 2 or more halogen atoms are combined with one C atom. Assuming that every element has a definite amt. of available energy of combination (affinity), there cannot be an absolute satn. of these affinities of the elements

within compds., for every reaction which compds. undergo depends upon the presence of some free energy, however small its amt. may be. The easy replaceability of the I in MeI is to be ascribed to the fact that the three H atoms arrogate affinities to themselves in combining. The residual energy of combination of the C atom, which is satd. by the I, is not equal to  $\frac{1}{4}$  of its total energy. The total affinities of the H atoms in  $\text{CH}_4$  are greater than that of the C atom, as indicated by the fact that Cl acting on  $\text{CH}_4$  gives at first chiefly MeCl and not equal amts. of  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  simultaneously, so that after substitution of one H atom the other 3 are held more firmly by the C; if now the 2nd, 3rd and 4th atom are substituted by halogen, the energy of combination set free for the halogen atoms is correspondingly more than 2, 3 and 4 times greater than that set free for the 1st halogen atom, *i. e.*, the firmness of the union of the halogen with the C atom increases with increasing substitution. In the halogen substitution products of hydrocarbons of the olefin series, in which the halogen is substituted directly on one of the unsatd. C atoms the halogen atom likewise exhibits an extraordinary sluggishness, and similar relations hold for the mono- and dihalogen derivs. of acetylene hydrocarbons; the halogen can to a great extent sat. its energy of combination at the expense of the C:C or C:C union and thus has but little partial affinity left available for other reactions. To clear up further these relationships attempts were made to replace the halogen atoms in  $\text{CHI:CHI}$  and  $\text{CHBr:CHBr}$  with  $\text{OEt}$ ,  $\text{OPh}$ ,  $\text{o-NaO}_2\text{CC}_6\text{H}_4\text{O}$ , amino groups,  $\text{SCN}$ , etc., but thus far, by the usual methods, it has in no case been possible to effect a substitution. In the present paper is reported the behavior of the *cis*- and *trans*- $\text{CHI:CHI}$  towards certain metals. With activated Mg they do not form a Grignard reagent but on gently warming on the  $\text{H}_2\text{O}$  bath they decomp. vigorously and quant. into  $\text{C}_2\text{H}_2 + \text{MgI}_2$ , an easily decompd. Grignard compd. probably being the primary product. When boiled in  $\text{Et}_2\text{O}$  with pulverized K, there is transiently formed a lachrymatory product of intensely penetrating odor, and  $\text{C}_2\text{H}_2$  is evolved. With Na in boiling  $\text{Et}_2\text{O}$ , the liquid isomer immediately, the solid form after some hrs., begins to deposit NaI, and if the reaction is stopped at the proper stage, there is obtained 1,1-diiodoethene (*asym-acetylene diiodide*) (A). The yield varies greatly with the length of reaction, as the A undergoes further decompn. under the long continued action of the Na; K. obtained about 50% A after 21 days from the solid and after 2 days from the liquid  $\text{CHI:CHI}$ . The I in A can be replaced by Cl or Br and the I set free by Br quant. detd. When exactly an equiv. amt. of Br is used, the resulting  $\text{C}_2\text{H}_2\text{Br}_2$  combines with another mol. to form a dimer, while with an excess of Br is obtained *acetylidene tetrabromide* (B),  $\text{CH}_2\text{BrCBr}_3$ , also formed from the dimer with excess of Br. Similarly, A with excess of Cl gives  $\text{ICl}_3$  and *acetylidene tetrachloride* (C). *trans*- $\text{CHI:CHI}$ , obtained in 125 g. yield from 180 g. I in 800 g. abs. alc. treated about 10 days with a slow current of  $\text{C}_2\text{H}_2$  purified as described in C. A. 13, 1825, sublimes in hollow needles, m.  $70^\circ$ , has a peculiar sharp odor, easily volatilizes with alc. vapor. *cis*-Isomer, obtained in 34% yield from  $\text{C}_2\text{H}_2$  at  $150-6^\circ$  b.  $185^\circ$ . A sublimes in thorn-like or pinnated crystals easily breaking up into an amorphous powder, has a penetrating, unbearable odor, is violently lachrymatory, m.  $56^\circ$ . Dimeric *asym-acetylene dibromide* (6.4 g. from 7.775 g. A in  $\text{CCl}_4$  and 4.4 g. Br exposed some hrs. to sunlight and heated 0.5 hr. on the  $\text{H}_2\text{O}$  bath), sublimes in yellowish leaflets of faint, not unpleasant odor, m.  $90^\circ$ , mol. wt. in freezing  $\text{C}_6\text{H}_6$  361; 4 g. heated several hrs. in  $\text{CCl}_4$  with excess of Br on the  $\text{H}_2\text{O}$  bath gives 5.8 g. B, brownish oil, mol. wt. in freezing  $\text{C}_6\text{H}_6$  354, has a faint  $\text{C}_6\text{H}_5$ -like odor, begins to decomp.  $175^\circ$ , carbonizes and evolves Br and HBr at  $215^\circ$ , b.  $107^\circ$  in *vacuo* (Siwoloboff method); it is also obtained in 5.4 g. yield from 5 g. A in 25 g.  $\text{CCl}_4$  and 9 g. Br boiled 8 hrs. and then exposed 2 hrs., with frequent shaking, to direct sunlight. C (4 g. from 7 g. A in  $\text{CCl}_4$  in direct sunlight treated 8 hrs. with a moderate current of dry, purified Cl), b.  $135^\circ$ , mol. wt. in freezing  $\text{C}_6\text{H}_6$  175. Like the sym. isomers, A is quant. decompd. by K or Mg in  $\text{Et}_2\text{O}$  into  $\text{C}_2\text{H}_2$  and the iodide of the metal. The 3 isomers (0.1 g. of each) in 3 cc. of  $\text{Et}_2\text{O}$  at  $23^\circ$  in

quartz cups exposed at a distance of 30 cm. to a Heraeus quartz lamp begin to deposit I in 5-10 min. and the decompn. (as measured by titration of the I) is complete in 8.5, 10.5 and 10 hrs. for *trans*-CHI:CHI, A and *cis*-CHI:CHI, resp. Action of zinc ethyl on the *cis-trans*-isomeric diiodoethenes. With F. SCHWEITZER. From 10 g. ZnEt<sub>2</sub> and 22.7 g. *trans*-CHI:CHI in 50 cc. Et<sub>2</sub>O heated 1 day in a sealed tube at 100°, then insolated 8 weeks with frequent shaking and poured into ice H<sub>2</sub>O are obtained C<sub>6</sub>H<sub>6</sub>, ZnI<sub>2</sub>, Zn(OH)<sub>2</sub> and 1.4 g. *trans*-1-iodobutene (A), faintly yellowish oil, mol. wt. in freezing C<sub>6</sub>H<sub>6</sub> 185.4-5.8, gradually loses I in the light, b<sub>10</sub> 57°, b. 127-8°, decomp. above 140° with liberation of I. *cis*-CHI:CHI, similarly treated, gives 3.5 g. A and 0.5 g. of the *cis*-isomer (B), b. 168°, B is probably the primary product and partially rearranges into A. A (1.5 g.) in 10 g. CCl<sub>4</sub> with 2 g. Br insolated 6 hrs. and then boiled 2 hrs. gives 1.6 g. 1,1,2-tribromobutane, faintly yellowish oil of sharp camphor-like odor, b<sub>14</sub> 98°, darkens on heating under atm. pressure, becomes opaque 220°, and decompd. with sepn. of Br, mol. wt. in freezing C<sub>6</sub>H<sub>6</sub> 298. Treated in dry Et<sub>2</sub>O with pulverized Na (frequently renewed) for 2 days, 3 g. A gives 1.6 g. 3,5-octadiene, faintly refractive liquid, b. 138-40°, gradually becomes yellowish in the air, mol. wt. in freezing C<sub>6</sub>H<sub>6</sub> 110; treated in cold CCl<sub>4</sub> with O<sub>3</sub>, it yields a yellowish red, thick, oily ozonide, which on decompn. with boiling H<sub>2</sub>O gives H<sub>2</sub>O<sub>2</sub>, EtCHO and (CHO)<sub>2</sub> and, on further treatment with boiling HNO<sub>3</sub>, (CO<sub>2</sub>H)<sub>2</sub> and EtCO<sub>2</sub>H. While the rearrangement of the *cis*- into the *trans*-CHI:CHI has been frequently observed, it has now been found that the *trans*-compd. heated in a sealed tube up to 190° decomp. slightly, with sepn. of I, and yields 45% of the *cis*-form. C. A. R.

Catalysis II. Dehydration and addition reactions of ethyl alcohol: formation of acetal and mercaptans. F. A. GILFILLAN. *J. Am. Chem. Soc.* 44, 1323-33(1922); cf. Johnson and Brown, *C. A.* 16, 10.—EtOH vapors alone or in the presence of CO<sub>2</sub> can be passed over pumice at 500° without appreciable decompn. Thoria can be inactivated for the dehydration of EtOH by strong calcination or by prolonged heating at a lower temp. Thoria does not exclusively dehydrate EtOH; under certain conditions a considerable amt. of AcH is produced by dehydrogenation. TiO<sub>2</sub> effected practically no dehydration of EtOH up to 355°. The blue oxide of W at lower temps. is a much more active catalyst for the production of C<sub>2</sub>H<sub>4</sub> than is thoria but at higher temps. they are practically of equal efficiency. No Et<sub>2</sub>O was produced in the presence of any of the catalysts. With thoria in the presence of CO<sub>2</sub> a considerable amt. of MeCH(OEt)<sub>2</sub> was formed. Pure dry CS<sub>2</sub> does not decomp. up to 400° over pumice or the blue W oxide; a trace of moisture, however, causes decompn. and the evolution of H<sub>2</sub>S. In the presence of any of the 3 metallic oxides mixts. of EtOH and CS<sub>2</sub> give considerable EtSH, TiO<sub>2</sub> proving the most efficient catalyst for this reaction. From EtOH and CS<sub>2</sub> were obtained high boiling liquids but in too small amt. for identification; no other evidence of the formation of esters of thiocarbonic acids was obtained. C. A. R.

Freezing points of organic substances. VI. New experimental determinations. J. TIMMERMANS AND TH. J. F. MATTAAR. *Bull. soc. chim. Belg.* 30, 213-9(1921); cf. *C. A.* 6, 174; 9, 9; 16, 2060.—The f. ps. of 73 compds. of the fatty series, liquid at the ordinary temp., including alkyl halides, ethers, ketones, acid anhydrides and chlorides, esters, and amines, are given in tabulated form with notes and references to earlier detns. where such have been made. The f. ps. given range from -13° to -140°. J. C. S.

Method of sudden pyrogenic decomposition, at high temperatures, of acetic acid. (MILLER) EGLANTINE PEYTRAL. *Bull. soc. chim.* 31, 113-8(1922).—AcOH freed from Ac<sub>2</sub>O by distn. was vaporized and passed through a Pt tube at 1150° at varying rates. At the rate of 0.097 g. per sec. for a week it gave no new products; at the rate of 0.083

g. per sec. three first-order reactions produce from AcOH the following:  $\text{Ac}_2\text{O}$ , CO,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and H. The  $\text{Ac}_2\text{O}$  then decomps. into  $\text{H}_2\text{O}$ , CO and  $\text{C}_2\text{H}_4$ . AcOH passed at the rate of 0.044 g. per sec., besides the above, gave also a further second-order reaction by decompn. of  $\text{C}_2\text{H}_4$  to produce H and  $\text{C}_2\text{H}_2$ . The slower rates of 0.035 g. and 0.02 g. per sec. increased the amts. of  $\text{C}_2\text{H}_2$ , CO and H through further reaction between  $\text{CO}_2$  and  $\text{CH}_4$  formed at slower gas velocities. B. V. BUSH

**Catalytic effect of ammonia on the oxidation of butyric acid with hydrogen peroxide.** E. J. WITZEMANN. *J. Biol. Chem.* 49, 123-41(1921).—No appreciable oxidation of  $\text{PrCO}_2\text{H}$  by  $\text{H}_2\text{O}_2$  occurs in the presence of from 0.2 to 4.0 equivs. of KOH but there is much oxidation when  $\text{NH}_4\text{OH}$  is present, increasing with increase in  $\text{NH}_4\text{OH}$  up to 4 equivs., after which it decreases somewhat because of the spontaneous liberation of  $\text{O}_2$  before it can be utilized in oxidation. If one equiv. of both  $\text{NH}_4\text{OH}$  and KOH is used more oxidation takes place than if two equivs. of either are added. This additive effect constitutes a chem. analogy to the biol. effects of certain mixed salts. The presence of  $\text{NH}_3$  in the soln. containing  $\text{PrCO}_2\text{K}$  and  $\text{H}_2\text{O}_2$  catalyzes the oxidation of  $\text{PrCO}_2\text{H}$  to  $\text{Me}_2\text{CO}$  and  $\text{CO}_2$ . The  $\text{NH}_3$  effect may be the agency by which the normal oxidation of fatty acids is brought about in the liver. This suggestion rests upon the fact that in the liver the substances required for this effect are all available and that this organ also normally shows the greatest tendency to form  $\text{AcCH}_2\text{CO}_2\text{H}$ . The results would tend to favor the view that the formation of  $\text{AcCH}_2\text{CO}_2\text{H}$  is a normal step in the oxidation of fatty acids and that in health it rapidly disappears but fails to break down further in acidosis of the diabetic type. A. P. LOTHROP

**Synthesis of  $\alpha$ -hydroxyisopentacosanic acid and its bearing on the structure of cerebronic acid.** P. A. LEVENE and F. A. TAYLOR. *J. Biol. Chem.* 52, 227-40(1922).—Cerebronic acid has been identified as  $\alpha$ -hydroxylignoceropentacosanic acid by conversion of both lignoceric acid from peanut oil and the tetracosanic acid from *d*-cerebronic acid (prepd. from brain cerebrosides) into *dl*- $\alpha$ -hydroxypentacosanic acids which were identical and by the conversion of lignoceric acid into cerebronic acid. The various derivs. obtained from cerebronic and lignoceric acids also had identical m. ps. The data furnished by Brigl (*C. A.* 10, 181) from which he concludes that cerebronic acid has the structure of a normal acid are quite inconclusive and there is doubt as to the purity of his prepn. The m. ps. of the new compds. prepd., detd. with a standardized Anschütz thermometer, were as follows: *isotricosanic acid*, 73.5°; *ethyl isotricosanate*, 55.5°; *isotricosyl alcohol*, 69°; *isotricosyl iodide*, 48°; *diethyl isotricosylmalonate*, 52.5°; *isotricosylmalonic acid*, 111°; *isopentacosanic acid*, 78.5°; *lignoceryl cyanide*, 56.5°;  *$\alpha$ -bromoisopentacosanic acid*, 70°; *dl-cerebronic acid* ( $\alpha$ -hydroxyisopentacosanic acid), 92.5°; *ethyl isopentacosanate*, 57°; *isopentacosyl alcohol*, 75°; *isopentacosyl iodide*, 51.5°; *isopentacosane*, 56°. A. P. LOTHROP

**The relations between fats and carbohydrates.** HANS MÜLLER. *Helvetica Chim. Acta* 5, 163-6(1922).—A résumé is given of the articles which have been published on the study of the intermediate products in the formation of carbohydrates from fats and fats from carbohydrates. ROGER ADAMS

**Preparation of acetic anhydride by the action of sulfur chloride on acetates.** MINORU MASHINO. *J. Chem. Ind. (Japan)* 24, 1023-39(1921).—Conditions for the max. yield of  $\text{Ac}_2\text{O}$  from NaOAc by use of S chlorides are investigated. The following are the best: Temp. 100°, reaction for 2 hrs., NaOAc is to be used in 2-6% excess over the theoretical value for  $\text{S}_2\text{Cl}_2$ , Sb as catalyzer (5% of the  $\text{S}_2\text{Cl}_2$ ). Under these conditions, 78.7% of NaOAc and 80.6% of S chlorides are utilized. If Sn, Fe, stibnite, or Fe sulfide is used instead of Sb, NaOAc is utilized to the extent of 57.2-68.8% and  $\text{S}_2\text{Cl}_2$  58.8-70.2%. If Mg and Zn are used, the yields are less than the amt. obtained without any catalyzer. Glacial AcOH,  $\text{Ca}(\text{OAc})_2$  and  $\text{NH}_4\text{OAc}$  cannot be substituted for

NaOAc for the prepn. of  $\text{Ac}_2\text{O}$  by this method.  $\text{SO}_2$  can be removed from the final product by distn.; Cl by NaOAc, and S by  $\text{HPO}_4$ . The cost of the chemicals in manufg. 100 kg. of  $\text{Ac}_2\text{O}$  (90% pure) is approx. \$85. According to M.  $\text{S}_2\text{Cl}_2$  acts on NaOAc and forms  $\text{AcCl}$ , which reacts with the excess of NaOAc to form  $\text{Ac}_2\text{O}$ . The catalyzer must first form a chloride with the  $\text{S}_2\text{Cl}_2$  and then help to form  $\text{AcCl}$ .

S. T.

**Catalytic decomposition of oleic acid.** ALPHONSE MAILHE. *Compt. rend.* 174, 873-4 (1922).—M. has shown (*C. A.* 16, 639) that catalytic decompn. of vegetable oils upon Cu-Mg, or Cu-Al gives liquid products transformed by hydrogenation upon Ni into satd. compds., acids and aliphatic, aromatic, and cycloaliphatic hydrocarbons, also rich gases, water and acrolein. Decompn. of the lower glycerides, triacetin, tributyrin, triisovalerin, gives a different reaction. Myristin and palmitin decomp. similarly to the oils. The production seems to be related to the richness in C of the acid constituting the glyceride. M. investigated the catalytic decompn. of higher fatty acids. Vapors of oleic acid (A) passed through a Cu tube enclosing pellets of Cu-Al at  $600-50^\circ$  decomp. normally giving liquid products, water and gas. The gas has the % compn.  $\text{CO}_2$  6.7, CO 10,  $\text{C}_2\text{H}_2$  10,  $\text{C}_2\text{H}_4$  11,  $\text{H}_2$  24. The liquid products are acids, giving with dil. soda a yellow amber colored product, begins to distil at  $40^\circ$ . The fractions are warmed strongly by  $\text{H}_2\text{SO}_4$  with absorption of more than half of the liquid. The portion b.  $40-50^\circ$  gives with Br amylene dibromide, heavy liquid, b.  $190-200^\circ$ . The entire neutral liquid formed by decompn. of A hydrogenated with Ni at  $180-200^\circ$  gives a colorless liquid of agreeable odor, not reacting with Br, sepd. by distn. into two series of products, b.  $40-150^\circ$ ,  $d_{10}$  0.7047-0.7636. Fraction  $60-75^\circ$  reacted only slightly with  $\text{H}_2\text{SO}_4\text{-HNO}_3$  and is mostly hexane. Fraction  $85-90^\circ$  by nitration and reduction gave  $\text{PhNH}_2$ , fraction  $105-110^\circ$  PhMe, identified by its di- $\text{NO}_2$  derivs. The residual liquid catalyzed upon Ni gave a small amt. of aromatic carbides, giving upon sepn. a residue  $d_{10}$  0.7090, near that of heptane. Fraction  $130-135^\circ$  similarly gives *m*-xylene and a liquid  $d_{10}$  0.7310, near that of nonane,  $d_{10}$  0.7228. The fraction b.  $150-250^\circ$  has a  $d_{10}$  0.8450. M. concludes that the catalytic decompn. of A gives rich gases, and liquid hydrocarbons, transformed by Ni hydrogenation into aliphatic and cyclic hydrocarbons, among them  $\text{C}_6\text{H}_6$ , PhMe, and *m*-xylene.

JAMES BROWN

**Erucic acid and its anhydride.** D. HOLDE AND C. WILKE. *Z. angew. Chem.* 35, 186-7 (1922); cf. *C. A.* 16, 1564.—An historical discussion of the methods of prepn. of erucic acid and its anhydride, with numerous references.

T. S. CARSWELL

**Molecular rearrangement of unsaturated compounds in acid solution.** ALF. GILLET. *Bull. soc. chim. Belg.* 30, 138-53 (1921); cf. Gillet, *C. A.* 16, 2107.—A theoretical discussion of some types of intramol. rearrangement which follow on dehydration. In certain of the examples quoted the rearrangement depends on the production of a bivalent C atom and its subsequent transformation with production of an ethylenic linking by the shifting of a group, while in others, *e. g.*, tert. alcs., it is impossible to interpret the mechanism of rearrangement in such a manner. The former case is referred to as the methylene, the latter as the ethylene, transformation. The conclusions, derived from the consideration of a variety of reactions, are embodied in the following rules: When a mono-substituted bivalent C atom results from dehydration, the most positive group attached to the next C atom moves from the latter to the former. The addn. of alkyl groups to unsatd. C atoms takes place in such a way as to produce the most sym. mol. possible by leaving the two C atoms taking part in the change with the greatest possible similarity in their attached groups. The converse holds for the subtraction of alkyl groups. In cases of ring formation where the C atoms concerned are not adjoining, the rule also obtains. Ethylenic transformation takes place most readily

when the H atom which is split off together with the OH group is linked to the C atom bearing the less positive groups (cf. Saytzev, *Ann.* 179, 296(1875)), and also if the OH group is attached to the more positively satd. C atom (cf. Markownikov, *Ann.* 153, 256(1869)). In the case of hydration of an ethylenic group, the rule also applies. When a ring is opened by taking up water, the break occurs between the two C atoms which are linked to the most unlike substituents, and the H atom combines with the more negatively, the OH group with the more positively, satd. of the two C atoms. The converse case, in which a ring is formed by dehydration, follows a similar rule. It is pointed out that this is only a special case, as  $C_2H_4$  itself may be regarded as a ring of two C atoms. The suggestion is made that org. groups should be arranged in an electropositive series. *Ibid* 226-52.—The general rules already enunciated (cf. above) are illustrated by numerous examples. The opening of a trimethylene ring by addn. of water or acids conforms with the rules referred to. Examples of the converse reaction are lacking, but the compd.  $CH_2:CMcMe:CH_2$ , which is the "normal" product of dehydration of pinacol, may be expected, owing to the negative character of the  $CH_2$  groups and the positive character of the intermediate groups, to undergo transformation into the following compds. in acid solns.:  $CH_2 \begin{array}{c} \diagup CMe \\ \diagdown CMe \end{array} CH_2 \longrightarrow HO-CMe \begin{array}{c} \diagup CMe \\ \diagdown CH_3 \end{array}$

$\longrightarrow O:CMcMeC_4$  (pinacolin). This explains the mechanism of the various transformations undergone by the pinacols and analogous compds., numerous examples of which are cited and classified. The various types of "ethylenic transformations" (*loc. cit.*), such as shifting of the double bond, addn. or subtraction of water or acids, and keto-enol rearrangements, and the mechanism of the dehydration of alcs., are discussed from the point of view of the general rules. Many of these cases are explained very simply, but for others the intermediate formation and rupture of one or two trimethylene rings is assumed. The type of transformation in any case depends chiefly on the constitution of the compd. and the electro-positive or -negative character of the radicals present. The catalyst as a rule plays a very subordinate part in detg. the character of the reaction.

J. C. S.

**Isomerism relations in the glutamic acid series.** FRANZ FEIST. *Ann.* 428, 25-40(1922); cf. C. A. 4, 1291; Thorpe, C. A. 6, 1150, 1151, 3408; 7, 337.—F. points out wherein his views differ from those of Thorpe and critically compares the two.

C. J. WEST

**$\beta$ -Phenyl- $\alpha$ -methylcarboxylglutamic acid ester and isomerism of the phenylglutamic acids.** F. FEIST, P. K. BREUER AND BERNH. LUBRICHT. *Ann.* 428, 40-59(1922).—The *trans*-ester seps. from petr. ether as monoclinic, holohedral crystals having the forms (001), (100), ( $\bar{1}01$ ), (110). The liquid *cis*-ester  $b_{14} 355^\circ$ . In order to det. the constitution the 2 esters were treated with  $O_3$  in AcOEt. Upon decompn. of the ozonide, both esters gave  $BzMe(CO_2R)_2$  and  $HCOCO_2R$ , or their hydrolytic or oxidation products. Sapon. of the esters leads to 2 phenylmethylglutamic acids and not 3 as Thorpe states. The pure *trans*-acid m.  $155^\circ$ , the *cis*-acid m.  $151^\circ$ . The free acids, on treatment with  $O_3$  and decompn. of the ozonides, give only  $BzOH$ ,  $(CO_2H)_2$  and AcOH. The di-Et esters yield definite products. The *trans*-diethyl ester,  $b_{14} 191-2^\circ$ , forms a normal ozonide,  $C_{16}H_{18}O_7$ , m.  $142^\circ$ , which may be recrystd. from AcMe. Decompn. with  $H_2O$  gave  $AcCO_2Et$ ,  $BzMeCHCO_2Et$  and  $BzCH_2CO_2Et$ . The acid fraction consisted principally of AcOH and PrOH. The *cis*-diethyl ester,  $b_{14} 184-5^\circ$ ,  $b_{14} 214^\circ$ ,  $b_{14} 220^\circ$ , likewise gave a solid ozonide, m.  $142^\circ$ . The decompn. products were similar to the above.

C. J. WEST

**The two  $\beta$ -methylglutamic acids.** F. FEIST AND P. K. BREUER. *Ann.* 428, 59-68(1922).—The decompn. of the ozonide of the *cis*-di-Et ester (Thorpe and Wood, C. A. 7, 1710; 8, 70) gave AcMe and  $AcCH_2CO_2Et$  as neutral products and AcOH and

(CO<sub>2</sub>H)<sub>2</sub> as acid products. The same products were obtained from the *trans*-ester. The action of Cl upon the *cis*-ester gave, in 1 expt., *ethyl dichloro-β-methylglutaconate*, orange-yellow oil, b<sub>12</sub> 159–61°, but usually a *trichloro derivative*, b<sub>0.17</sub> 116.5°, b<sub>0.36</sub> 130°, b<sub>1.75</sub> 142°, b<sub>2.70</sub> 155°, b<sub>11</sub> 169–71°. The *dibromo ester* b<sub>0.11</sub> 108°, b<sub>0.36</sub> 116°, b<sub>2.25</sub> 133°, b<sub>11</sub> 154–6°, b<sub>12</sub> 159–60°. The action of CHNa(CO<sub>2</sub>Et)<sub>2</sub> leads to the formation of [CH(CO<sub>2</sub>Et)<sub>2</sub>]<sub>2</sub> and *diethyl oxalbutyrate* (?), b<sub>1.4</sub> 125.3° (some decompn.). C. J. WEST

*α,β-Dimethylglutaconic acid*. F. FEIST AND P. K. BREUER. *Ann.* 428, 68–75 (1922); cf. *Ann.* 345, 117.—The *trans*-ester does not add O<sub>2</sub> as easily as the *cis*-ester. The decompn. products consisted of AcCH<sub>2</sub>CO<sub>2</sub>Me, MeAcCHCO<sub>2</sub>Me, the former predominating, and AcMe. C. J. WEST

Several transformations of ethyl' *γ*-bromo-*α,γ*-dicarboxyglutaconate. FRANZ FALTIS AND CARLA RUIZ DE ROSAS. *Monatsh.* 42, 459–70 (1922).—(EtO<sub>2</sub>C)<sub>2</sub>C·CHCBr·(CO<sub>2</sub>Et)<sub>2</sub> (A) (C. A. 4, 2281), prepd. quant. by the action of 3 atoms Br upon (EtO<sub>2</sub>C)<sub>2</sub>C·CHC(CO<sub>2</sub>Et):C(OCu)OEt in CHCl<sub>3</sub>, decomp. when distd. *in vacuo* and when warmed for some time on the H<sub>2</sub>O-bath, probably because of the HBr which is split off. Vacuum distn. gave a green, fluorescent oil, *triethyl' γ-hydroxy-α,γ-dicarboxyglutaconic lactone* (B), b<sub>16</sub> 212–6°, solidifying to a colorless mass, m. 28–30°. This does not give a reaction with FeCl<sub>3</sub> nor does it form a Cu salt. With EtOK the lactone grouping is not opened but EtCO<sub>2</sub> is split off, forming the compound C<sub>14</sub>H<sub>11</sub>O<sub>6</sub>K, cubes, does not m. 300°, gives with FeCl<sub>3</sub> an intense indigo-blue ppt., and forms a complex orange-red Cu salt. The action of Et<sub>2</sub>NPh upon A leads to a mixt. of products, 1 of which probably is B. The action of 1 mol. EtOK upon A yields a product, as yet not identified, probably formed by sapon. and splitting off of CO<sub>2</sub>, which gives an intense blue-violet FeCl<sub>3</sub> reaction and gives a Br-containing Cu salt. C. J. WEST

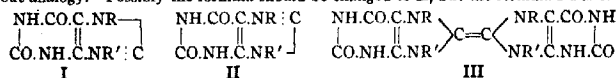
*α-Hydroximinoketones, cobaltous salts*. G. PONZIO. *Gazz. chim. ital.* 52, I, 285–8 (1922).—P. has prepd. Co'' salts of *α*-hydroximinoketones, stated to be impossible to prep. by Chugaev. Comps. of the type R'CO C(:NOH)COR'' and R'COC(:NOH)H, where R' and R'' represent Me or Ph, if treated in H<sub>2</sub>O or alc. with aq. (AcO)<sub>2</sub>Co give Co'' and not Co''' salts. They are all more or less sol. in org. solvents, from which they sep. in well defined crystals they possess an abnormal dark red color; the powdered crystals are orange-red; they give none of the reactions of Co ions. Therefore they must be considered as complex

salts of the type  $\left[ \begin{array}{c} \text{R}'\text{C}:\text{NO} \\ | \\ \text{R}'\text{C}=\text{O} \end{array} \right]_2 \text{Co}$ . P. has also prepd. Co\* salts of (MeCO)<sub>2</sub>C:NOH

and PhCOC(:NOH)H and confirmed the existence of the Co'' salts of *α*-PhCOC(:NOH)Ph. *Cobaltous isonitrosoacetylacetone*, [(MeCO)<sub>2</sub>C:NO]<sub>2</sub>Co, seps. in brick-red flakes on mixing aq. (MeCO)<sub>2</sub>C:NOH with (AcO)<sub>2</sub>Co and warming slightly; from ligroin it crysts. in blood-red prisms, m. 164°, sol. in cold alc., Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, Me<sub>2</sub>CO, CHCl<sub>3</sub>, very slightly sol. in petr. ether, appreciably in warm and slightly in cold ligroin, somewhat in boiling 50% AcOH, easily in concd. H<sub>2</sub>SO<sub>4</sub> and in NaOH and NH<sub>4</sub>OH with a dark rose-red color, slightly in H<sub>2</sub>O, the soln. giving no reactions of Co ions. *Cobaltous isonitrosobenzoylacetone*, from alc. MeCOC(:NOH)COPh and (AcO)<sub>2</sub>Co, dark orange needles, m. 220° (decompn.), almost insol. in hot alc., Et<sub>2</sub>O, ligroin and 50% AcOH, sol. in cold C<sub>6</sub>H<sub>6</sub> and CHCl<sub>3</sub>, quite sol. in hot and slightly in cold Me<sub>2</sub>CO, from which it may be recrystd., insol. in H<sub>2</sub>O, sol. in cold H<sub>2</sub>SO<sub>4</sub> and in NaOH and NH<sub>4</sub>OH. *Cobaltous isonitrosoacetophenone*, from aq. alc. PhCOC(:NOH)H warmed with (AcO)<sub>2</sub>Co, dark orange plates from C<sub>6</sub>H<sub>6</sub>, begins to decomp. 100–20°, the decompn. becoming violent at about 240° and BzOH subliming; it is slightly sol. in alc., Et<sub>2</sub>O and Me<sub>2</sub>CO, sol. in cold CHCl<sub>3</sub>, very sol. in hot and less in cold C<sub>6</sub>H<sub>6</sub>, insol. in H<sub>2</sub>O, ligroin, NaOH and NH<sub>4</sub>OH, sol. in cold concd. H<sub>2</sub>SO<sub>4</sub> with red-orange color, somewhat sol. in boiling 50% AcOH, from which it crysts. on cooling. *Cobaltic bensil α-monooxime*, [Ph(PhCO)-

$C:NO_2)_2Co$ , obtained but not described by Chugaev, seps. on warming alc.  $\alpha$ -PhCOC $:(NOH)Ph$  with aq.  $(AcO)_2Co$ , dark red prisms from  $Me_2CO \cdot CHCl_3$ , decomp.  $195^\circ$ , sol. in cold  $CHCl_3$  and  $C_6H_6$ , slightly in alc.,  $Et_2O$ ,  $Me_2CO$ , ligroin and boiling  $AcOH$ , insol. in  $KOH$  and  $NH_4OH$ , sol. in cold concd.  $H_2SO_4$ . *Cupric isonitrosoacetylacetonate*, from alc.  $(MeCO)_2C:NOH$  and  $(AcO)_2Cu$ , olive-green powder insol. in  $H_2O$  and the common org. solvents, decomp. violently  $140^\circ$ , sol. in  $NaOH$ ,  $NH_4OH$ , dil.  $HCl$  and dil.  $AcOH$ ; as it gives several reactions of  $Cu^{++}$  ions, it must be considered as a less stable complex salt than the  $Co^{++}$  salts of the  $\alpha$ -hydroximinoketones. A. W. CONTIERI

**7,9-Dialkyldeoxyuric acids.** I. HEINRICH BILTZ. *Ann.* **426**, 237-46(1922); *J. Chem. Soc.* **122**, 380-1.—7,9-Dialkyl-8-thiouric acids (A), which are obviously incapable of being converted into xanthines by the method previously employed (Biltz and Strufe, *C. A.* **15**, 2834) and cannot readily be converted into the uric acids by oxidation, pass, on treatment with mild oxidizing agents, into substances termed deoxyuric acids, containing 1 atom O less than the corresponding uric acids. They are more strongly basic than the uric acids and are characterized by forming sparingly sol. salts with  $HCl$ . A convenient method of prepn. consists in oxidizing by means of I a soln. of the Na salt of A, rendered alk. by  $NaHCO_3$ ; usually the peroxide of the deoxyuric acid is pptd.  $HNO_3$  also converts A into the deoxyuric acid. These acids are remarkably resistant to oxidizing and reducing agents in acid and alk. solns. The product obtained by the action of  $Cl-H_2O$  gives the murexide test with  $NH_3$  and the periodide, when heated with  $NaOH$ , decomp., with the formation of a moderate amt. of the corresponding dialkyluric acid. With aq.  $Ba(OH)_2$  hydrolysis occurs, forming a formyldialkylidaminouracil, from which the CHO group may be eliminated by  $HCl$ . The free dialkylidaminouracil (B) may be reformylated, with  $HCO_2H$ , and the formyl compd. dehydrated with the formation of the original deoxyuric acid. B with  $ClCO_2Et$  gives a urethan, from which the uric acid may be prepd. by the usual reactions. The constitution suggested for the deoxyuric acids (I) is a remarkable one, inasmuch as it involves a 5-valent N and the presence of a triple linking in a ring, but it appears not to be without analogy. Possibly the formula should be changed to II, but the formula III is out



of the question by reason of the mol. wt. and on obvious chem. grounds. II. **7,9-Dimethyldeoxyuric acid.** H. BILTZ and HANS BÜLOW. *Ibid* 246-63.—7,9-Dimethyl-8-thio- $\psi$ -uric acid (C) is readily prepd. from 7-methyluracil (D) and methylthiocarbimide (D'), 4-sided prisms from  $H_2O$ , m.  $224^\circ$  (cor., decompn.). A small amt. of 7,9-dimethyl-8-thiouric acid (E) is formed as a by-product in this condensation and may be obtained in good yield from C by boiling with 10%  $HCl$ , needles, m.  $362^\circ$  (decompn.) and sol. in about 600 parts boiling  $H_2O$ . 7,9-Dimethyldeoxyuric acid (F) may be prepd. from E by either of the general methods described above and is sol. in about 4 parts boiling  $H_2O$ , from which it forms needles, decomp.  $385^\circ$ . *Hydrochloride*, decomp.  $345-50^\circ$ ; *perchlorate*, decomp.  $270^\circ$ ; *acid sulfate*, decomp.  $265^\circ$ ; *nitrate*, decomp.  $205^\circ$ ; *iodide*, decomp.  $350^\circ$ ; *periodide*, dark brown needles, decomp.  $180-210^\circ$ ; *chloroaurate*, decomp.  $288-96^\circ$ ; *chloroplatinate*, and an additive product with silver nitrate,  $2C_7H_9O_2N_4 \cdot AgNO_3(?)$ . Heating with S converts F into E, while I and alkali hydroxides form 7,9-dimethyluric acid. 6-Methylamino-5-formylmethylaminouracil, decomp.  $385^\circ$ , can be crystd. from 20 parts of boiling  $H_2O$  or from  $AcOH$ , from which it seps. with 2  $AcOH$  of crystn. 5,6-Dimethyldiaminouracil, rhombic plates with 2  $AcOH$  from  $AcOH$ , decomp.  $380^\circ$ , gives a *hydrochloride*, decomp.  $261^\circ$ . With  $ClCO_2Me$  a *methyl carbamate* is formed, sol. in 60 parts  $H_2O$  and decomp.  $343^\circ$ . *Ethyl ester*, decomp.  $325^\circ$ , is sol. in 10 parts boiling  $H_2O$ . III. **7-Methyl-9-ethyldeoxyuric acid.**



*Ibid* 284-9.—7-Methyl-*g*-ethyl-8-thio- $\psi$ -uric acid, from D and ethylthiocarbimide, hexagonal tablets, decomp. 206°. The thiouric acid, silky needles, decomp. 359°, and sol. in about 400 parts boiling H<sub>2</sub>O. 7-Methyl-*g*-ethyldeoxyuric acid, leaflets with 2H<sub>2</sub>O, decomp. 325°; hydrochloride, decomp. 277-78°; iodide, decomp. 254°; periodide, decomp. 215°; chloroaurate, decomps. 190°; complex silver nitrate salt. IV. 9-Methyl-7-ethyldeoxyuric acid. H. BILTZ AND DOROTHEA HEIDRICH. *Ibid* 289-83.—9-Methyl-7-ethyl-8-thio- $\psi$ -uric acid, leaflets, m. 212° (decompn.), is difficult to isolate owing to the ease with which it undergoes conversion into *g*-methyl-7-ethyl-8-thiouric acid, silky, filamentous crystals, decomp. 344°. 9-Methyl-7-ethyldeoxyuric acid, rectangular leaflets with 2H<sub>2</sub>O, decomp. 340°; hydrochloride, decomps. 263°; iodide, decomps. 251°; periodide, C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>N<sub>4</sub>HI<sub>2</sub>, decomps. 215-22°; periodide, C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>N<sub>4</sub>HI<sub>2</sub>, decomps. 230-35°; perchlorate, decomps. 238°; nitrate, decomps. 194°; chloroaurate, decomps. 239°; complex potassium triiodide salt, C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>N<sub>4</sub> KI<sub>3</sub>, decomps. 242°. 6-Methylamino-5-formyl-ethylaminouracil, best obtained by using Ca(OH)<sub>2</sub>, hexagonal crystals, decomp. 262° and very sol. in H<sub>2</sub>O. 6-Methylamino-5-ethylaminouracil, long needles, m. 235° (decompn.); hydrochloride decomps. 280°; methyl carbamate, by the action of ClCO<sub>2</sub>Me, m. 326° (decompn.). 9-Methyl-7-ethyluric acid, small, lancet-like leaflets, m. 355° (decompn.); with Cl-H<sub>2</sub>O, it yields 4,5-dihydroxy-9-methyl-7-ethyl-4,5-dihydrouic acid, small elongated prisms, m. 240° (decompn.). 4-Hydroxy-5-methoxy derivative, m. 131°, and 4-hydroxy-5-ethoxy derivative, m. 193°, are prepd. from the uric acid by means of Cl and MeOH or EtOH. V. 1,7,9-Trimethyldeoxyuric acid. H. BILTZ AND HANS BÜLOW. *Ibid* 283-90.—1,7,9-Trimethyl-8-thio- $\psi$ -uric acid, from 1,7-dimethyluramil and D', small, thick crystals, decomp. 185° and give 1,7,9-trimethyl-8-thiouric acid, m. 317°, on heating with HCl, also prepd. from 7,9-dimethylthiouric acid with Me<sub>2</sub>SO<sub>4</sub>. 1,7,9-Trimethyldeoxyuric acid (G), small rhombic leaflets with 1H<sub>2</sub>O, m. 348° (decompn.); hydrochloride, filamentous needles, decomp. 231°; iodide, glistening, rectangular leaflets, decomp. 249°; periodide, sinters 208°; nitrate, sinters 125°; chloroaurate, needles, decomp. 267°. 6-Methylamino-5-formylmethylamino-3-methyluracil, rectangular tablets, sinters 267°, evolving H<sub>2</sub>O vapor and giving G. VI. 1,3,7,9-Tetramethyldeoxyuric acid. H. BILTZ AND D. HEIDRICH. *Ibid* 290-99.—1,3,7,9-Tetramethyl- $\psi$ -uric acid, decomps. 165°, is prepd. from 1,3,7-trimethyluramil and D', or from C and Me<sub>2</sub>SO<sub>4</sub>. It passes very easily into 1,3,7,9-tetramethylthiouric acid, fine needles, m. 255-8° (decompn.). Methylation of 1,3,7-trimethyl-8-thiouric acid with Me<sub>2</sub>SO<sub>4</sub> and NaOH leads to the formation of the 8-methylthiol ether, m. 179-80°, which appears to possess no tendency to pass into the isomeric C-Me deriv. 1,3,7,9-Tetramethyldeoxyuric acid, m. 282°, forms a hydrochloride, m. 110-15°; a perchlorate, decomps. 237°; an iodide, decomps. 238°; and a periodide, m. 195°; on hydrolysis with Ba(OH)<sub>2</sub> it yields 6-methylamino-5-formylmethylamino-1,3-dimethyluracil, small, elongated prisms from EtOH, decomp. 259-60°. 5,6-Dimethylamino-1,3-dimethyluracil, decomps. 290°, is unstable in the presence of air and moisture; hydrochloride, prisms, decomp. 278°. VII. 7,9-Diethyldeoxyuric acid. H. BILTZ AND H. BÜLOW. *Ibid* 299-305.—7,9-Diethyl-8-thio- $\psi$ -uric acid, leaflets, decomp. 208°. 7,9-Diethyl-8-thiouric acid, decomps. 340-69°, is sparingly sol. in boiling H<sub>2</sub>O and does not give the murexide reaction. 7,9-Diethyldeoxyuric acid, rectangular leaflets with 1H<sub>2</sub>O, decomps. 305-7°, and forms an iodide, rectangular leaflets, m. 262° (decompn.); a periodide, brown needles, m. 225° (decompn.); and a chloroaurate, decomps. 180-90°. 6-Ethylamino-5-formylethylaminouracil, needles, decomp. 268°, with evolution of H<sub>2</sub>O and formation of the original deoxyuric acid.

C. J. WEXR

9-Methyl-8-iodo- $\Delta^{7,8}$ -isoxanthine. H. BILTZ AND HANS BÜLOW. *Ann.* 426, 306-12(1922); cf. preceding abstr.—The S atom in 9-methyl-8-thiouric acid (A) is removed by I and NaHCO<sub>3</sub>, the product being a polyiodide of 8-iodo-9-methyl- $\Delta^{7,8}$ -iso-

*xanthine*, from which the free base is liberated by  $\text{H}_2\text{SO}_4$ . It seps. from 800–900 parts boiling  $\text{H}_2\text{O}$  in short, thick crystals, which begin to lose I at  $280^\circ$ . *Ammonium salt*,  $\text{C}_8\text{H}_6\text{O}_4\text{N}_4\cdot\text{NH}_4\cdot 2\text{H}_2\text{O}$ ; *diiodide*,  $\text{C}_8\text{H}_4\text{O}_4\text{N}_4\text{I}_2$ . Reduced with  $\text{SnCl}_2$  it gives 9-methyl- $\Delta^{7,8}$ -isoxanthine, conveniently isolated as the *chlorokannite*,  $(\text{C}_8\text{H}_6\text{O}_3\text{N}_4)_2\cdot\text{H}_2\text{SnCl}_4$ . Methylation of A with  $\text{Me}_2\text{SO}_4$  and KOH gives 8-methylthiol-9-methyl- $\Delta^{7,8}$ -isoxanthine, fine needles or 4-sided leaflets, decomp.  $335^\circ$ . C. J. WAST

**Solution equilibriums of the desmotropisomeric diacetosuccinic esters and their colorimetric determination.** L. KNORR AND H. P. KAUFMANN. *Ber.* 55B, 202–48 (1922).—Of the 13 possible isomeric di-Et diacetosuccinates (4 stereoisomeric diketo forms resulting from the presence of the 2 asym. C atoms, 3 *cis-trans*-isomeric dienols and 2 *cis-trans*-isomeric keto-enols, each of the last 2 being theoretically capable of existence in a *d*-, a *l*- and a *dl*-form), the following 5 are known:  $\beta$  (diketo), m.  $89^\circ$  (A);  $\gamma$  (diketo), m.  $30^\circ$  (B);  $\alpha$  (dienol), m.  $45^\circ$  (C);  $\alpha_1\beta$  (keto-enol), liquid (D); and  $\alpha_2\beta$  (keto-enol), m.  $20^\circ$  (E). For these substances the colorimetric estimation of the color of the Fe salts of the enol forms gives sufficiently accurate results. In detg. the extent and velocity of enolization, practically the same method as K. and Schubert's (*C. A.* 6, 90) was used. All the rearrangement expts. were carried out at  $30^\circ$  in 0.1 *N* solns., small portions of which were dild. with alc. and the necessary amt. of 0.1 *N* alc.  $\text{FeCl}_3$  and compared colorimetrically with a standard soln. of known enol content. At first the Fe salts of the ester were used for the standards; the Cl-free salt is red-brown and, owing to the action of the small amt. of  $\text{H}_2\text{O}$  present in the  $\text{FeCl}_3$  used in its prepn., has not the expected compn.  $\text{Fe}_2\text{R}_4$  but appears to be of basic nature (found, 17% Fe). The *chloroferic* salt, which is of greater importance for the colorimetric detns. and is obtained as a deep violet, unstable powder with excess of  $\text{FeCl}_3$  in  $\text{Et}_2\text{O}$ , apparently has the constitution  $[\text{Cl}_2\text{FeOCMe:C}(\text{CO}_2\text{Et})_2]_n$ . Pure enols treated with alc.  $\text{FeCl}_3$  to max. color intensity give the same color intensity as an equal column of a soln. of the above Fe salt (to which has been added an amt. of alc. HCl equiv. to that liberated from the enol according to the equation  $2\text{FeCl}_3 + \text{RH}_2 = \text{R}(\text{FeCl}_2)_2 + 2\text{HCl}$ ), and the keto-enol C gives the same color intensity as a layer half as deep of the soln. of the Fe salt. In detg. rearrangement velocities or the enol content at equil., therefore, either the Fe salt (+HCl) or the enol (+ $\text{FeCl}_3$ ) may be used, but as the solns. retain their color only for a limited time it is simpler to use a stock alc. equil. soln. of known enol content and prep. a fresh standard soln. for every measurement by adding alc.  $\text{FeCl}_3$ . To avoid an excess of  $\text{FeCl}_3$  in the unknown solns. the amt. necessary to produce the max. color intensity is detd. in preliminary expts. and this amt. is added in one portion in making the final measurement. Where other solvents than EtOH are used in the unknown soln. a small sample of the latter is dild. to a known vol. with alc. and  $\text{FeCl}_3$  and the corresponding amt. of the other solvent is added to the alc. standard soln. *Influence of dissociating power of the solvent.*—The enolization const.  $K_1+K_2$  (time in days) at  $30^\circ$  of A is 4.964, 4.656, 0.119, 0.057 in MeOH, EtOH,  $\text{Me}_2\text{CO}$  and  $\text{CHCl}_3$ , resp.; in hexane,  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$  the enolization is so extraordinarily slow that the consts. could not be detd. *Influence of temp. on the velocity of rearrangement and on the equil.* The velocity of rearrangement increases with the temp. but the relative amts. of enol and ketone at equil. are not appreciably different at  $30^\circ$  and at the b. p. *Influence of concn.*—Within not too wide limits of concn. neither the velocity of rearrangement nor the concn. of enol at equil. is much affected by the concn., as shown by the following amts. of enol found in 0.2, 0.1 and 0.05 *N* soln., resp. in MeOH after various time intervals at  $30^\circ$ : 2.5 hrs., 4, 4.2, 4.8; 4 hrs., 5.5, 5.8, 6.1; 8 hrs., 7.7, 8, 8; 14 hrs., 10.0, 10, 10. *Influence of dissociating power of the solvent on the equil.*—HCl and EtOH solns. show about the same % of enol at equil., MeOH somewhat less than the higher alcs. Colorimetric detns. on equil. solns. in hexane prepd. by letting stand

1 year at room temp. or heating a long time in sealed tubes at 100° gave unusually high amts. of enol, which led to the suspicion that the dienol C, which thus far had never been detected in melts or equil. solns., might be present in the hexane soln. and as a matter of fact mechanical sepn. of the isomers led to its detection. So, also, C was detected in a concd. Et<sub>2</sub>O soln. of A heated 1 month in a sealed tube at 100°. In view of this discovery, the values given above for the % of enol detd. colorimetrically refer only to the % of enol "groups"; i. e., 15% enol may mean 15% dienol or 30% keto-enol.

C. A. R.

**Function of phosphates in the oxidation of glucose by hydrogen peroxide.** ARTHUR HARDEN AND F. R. HENLEY. *Biochem. J.* 16, 143-7(1922).—The oxidation of glucose by H<sub>2</sub>O<sub>2</sub> takes place in presence of the following buffer substances: NaHCO<sub>3</sub> + CO<sub>2</sub>, Na<sub>2</sub>HAsO<sub>4</sub> + NaH<sub>2</sub>AsO<sub>4</sub>, NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, K<sub>2</sub>HPO<sub>4</sub> + KH<sub>2</sub>PO<sub>4</sub>, provided the *p*<sub>H</sub> does not rise much above 7.3. The stability of aq. H<sub>2</sub>O<sub>2</sub> is increased by the presence of phosphates.

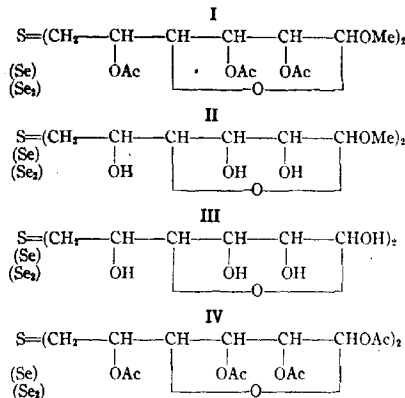
BENJAMIN HARROW

**Formation of formic acid in the degradation of glucose in alkaline solution.** H. I. WATERMAN AND M. J. VAN TUSSENBROEK. *Chem. Weekblad* 19, 135-6(1922).—Exptl. proof was adduced to show that in the degradation of glucose in normal NaOH, HCO<sub>2</sub>H is formed; this confirms the work of Meisenheimer (*C. A.* 2, 1894). CO<sub>2</sub> is only formed later and not in the early stages.

VINCENT VERMOOTEN

**Synthesis of disaccharides containing sulfur and selenium by the union of two glucose radicals through the 6-C atoms.** A new derivative of 6-bromoglucose. F. WREDE. *Z. physiol. Chem.* 115, 284-304(1921); cf. *C. A.* 15, 2837.—Pentaacetylglucose (50-100 g. quantities) together with a suitable quantity of HBr were sealed in glass tubes with the aid of a CO<sub>2</sub>-Et<sub>2</sub>O mixt. and a vacuum and then allowed to stand at room temp. for 8 days. From the product obtained the triacetate of Me glucoside 6-bromohydrin was prepd. in the usual manner, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -7.78°. Et triacetylglucoside 6-bromohydrin, prepd. by treating 10 g. of the acetate in abs. alc. with 6 g. Ag<sub>2</sub>CO<sub>3</sub> for 6 hrs., warming to dissolve the glucoside, filtering and recrystg. *in vacuo*, m. 154°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> -11.70° to 11.78° (in EtOAc). Treatment with NH<sub>3</sub> in MeOH for 10 hrs. at 0° eliminates the Ac groups.  $\alpha$ -Tetraacetyl-6-bromoglucose was prepd. by treating the acetodibromoglucose with a 3-fold wt. of Ac<sub>2</sub>O contg. ZnCl<sub>2</sub>. On pouring into H<sub>2</sub>O it pptd. in cryst. form, m. 171°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> 107.2-7.9° (in EtOAc). I was prepd. by treating 2 g. Me triacetylglucoside 6-bromohydrin with 40 cc. 96% alc. contg. K<sub>2</sub>S sealed in glass and half immersed in an oil bath at 170° for 2 hrs. The alc. was evapd. *in vacuo* and the residue heated with 20 cc. Ac<sub>2</sub>O for 1.5 hrs. at 100°. After adding 30 cc. of alc. most of the Ac<sub>2</sub>O distills off as EtOAc. The residue was treated with 50 cc. of warm water for two hrs. and then taken up with 50 cc. Et<sub>2</sub>O. After drying the Et<sub>2</sub>O soln. I crystd., m. 168°, [ $\alpha$ ]<sub>D</sub><sup>15</sup> -10.51° (in EtOAc), sol. in CHCl<sub>3</sub>. No mutarotation was observed. The deacetylated compd. (II) was obtained by treatment with NH<sub>3</sub> in MeOH for 15 hrs. at 0°. The residue after evapn. *in vacuo* was dissolved in 90% alc. and Et<sub>2</sub>O was added until pptn. began; it m. 188°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> 6.39-6.66°, sol. in H<sub>2</sub>O and hot alc. To prepare diglucosyl 6-sulfide (III) the Me groups were split off with 5% H<sub>2</sub>SO<sub>4</sub> in a sealed tube at 100° for 3 hrs. After removing the H<sub>2</sub>SO<sub>4</sub> with BaCl<sub>2</sub> and filtering through kieselguhr the soln. was evapd. and the residue dissolved in alc. It was re-filtered and evapd., again dissolved in alc. and pptd. with Et<sub>2</sub>O; it sinters 135°, m. 150°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> 80.9°, sol. in H<sub>2</sub>O and dil. alc. It shows no mutarotation, forms an osazone and reduces Fehling soln. Octaacetyldiglucosyl 6-sulfide (IV) was obtained by treating 0.5 g. of the sulfide with 5 cc. Ac<sub>2</sub>O and 7 cc. pyridine for 48 hrs. at 0°. On adding H<sub>2</sub>O the compd. pptd. and was extd. with Et<sub>2</sub>O. The Et<sub>2</sub>O soln. after concn. was treated with petroleum ether until pptn. began. It crystd. on standing, m. 163° (not sharply), by [ $\alpha$ ]<sub>D</sub><sup>15</sup> 56.2° (in EtOAc), sol. in most org. solvents. The mono-Se derivs. corresponding

to the S compds. described were prepd. analogously. For prepg. the di-Se compds. cf. *C. A.* 14, 1546. The mono-Se compd. of I m. 179–80°,  $[\alpha]_D^{16}$   $-3.1^\circ$  (in EtOAc); of (II) m. 138°,  $[\alpha]_D^{14}$  14.58; diglucosyl 6-selenide sinters 160° and decomp. 200°,  $[\alpha]_D^{14}$  69.5–70.3°; octaacetyldiglucosyl 6-selenide m. 150–5°,  $[\alpha]_D$  40° (in EtOAc). The di-Se compd. of I m. 148°,  $[\alpha]_D^{18}$  49.4–49.7° (in EtOAc); of II sinters and then m. 96–7°,  $[\alpha]_D^{14}$  75.7–6.3°; diglucosyl 6-diselenide decomp. 125°,  $[\alpha]_D^{14}$  139.3–145.6°; octaacetyldiglucosyl 6-diselenide sinters and then m. 175–9°.

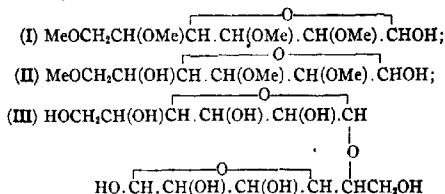


R. L. STEHLE

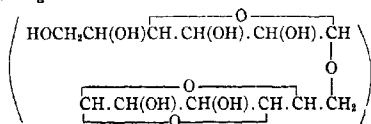
**Polymerization of l-glucosan.** AMÉ PICTET AND J. H. ROSS. *Compt. rend.* 174, 1113–4 (1922).—A preceding note [*Compt. rend.* 173, 158 (1921)] discussed the effect of pressure upon the polymerization of glucosan. The same effect has been detd. with its isomer, *l*-glucosan (A). A warmed to 140° with a trace of ZnCl<sub>2</sub> gives the reaction  $n \text{ C}_6\text{H}_{10}\text{O}_5 = (\text{C}_6\text{H}_{10}\text{O}_5)_n$  but the products differ according to the pressure. *N* increases with the pressure, taking the values 2, 4, 6, and 8. P. and R. synthesized thus a series of poly-*l*-glucosans comparable and parallel to the series of polyamyloses given by the decay of starch under the influence of *Bacillus macerans*. With 15 mm. Hg pressure was obtained a di-*l*-glucosan ( $\text{C}_6\text{H}_{10}\text{O}_5$ )<sub>2</sub> (B) distinguished from A by its insoly. in acetone, and purified by soln. in AcOH and pouring into 3–4 vols. of acetone; it ppts. as a white amorphous powder of slightly sweetish taste, easily sol. in 95% alc., and pptd. by cooling, very sol. in H<sub>2</sub>O, AcOH and pyridine, but insol. in the other usual solvents; mol. wt. in freezing H<sub>2</sub>O, 322 (calcd. 324),  $[\alpha]$  28.2° (polymerization of A causes a change of sign). The same operation at atm. pressure gives almost exclusively a tetra-*l*-glucosan ( $\text{C}_6\text{H}_{10}\text{O}_5$ )<sub>4</sub>, purified by soln. in a small amt. of H<sub>2</sub>O and addition of alc., tastes flat, not sweet, very sol. in H<sub>2</sub>O, quite sol. in pyridine, insol., even hot, in MeOH, EtOH, and other org. solvents, mol. wt. 640 (calcd. 648),  $[\alpha]$  111.9°. In order to study higher pressures, P. and R. warmed A in sealed tubes, in presence of a volatile liquid inactive toward A and ZnCl<sub>2</sub> of known vapor pressure at 140°. By use of C<sub>6</sub>H<sub>6</sub> (4.6 atm.) was obtained a hexa-*l*-glucosan ( $\text{C}_6\text{H}_{10}\text{O}_5$ )<sub>6</sub>, white amorphous substance, very sol. in H<sub>2</sub>O, pptd. by adding a small amt. of alc., distinguished by its insoly. in pyridine, and mol. wt. (found 964, calcd. 972),  $[\alpha]$  94.1°. By use of Et<sub>2</sub>O of vapor pressure 13 atm. at 140°, octo-*l*-glucosan, ( $\text{C}_6\text{H}_{10}\text{O}_5$ )<sub>8</sub>, was formed, whose soly. is the same as the hexa-isomer, but mol. wt. 1318 (calcd. 1296),  $[\alpha]$  94.1°. The last three polymers have not sharp m. ps.; decomp. 195–200°, have an insipid taste, are not colored by I. One

concludes that by polymerization at const. temp., but increasing pressures, A gives products with properties approaching those of dextrin; this is of interest in the mechanism of the transformation of sugar into starch in plants, occurring in cells where high pressures prevail, higher, perhaps, than those of these expts. JAMES BROWN

**Constitution of starch and glycogen.** P. KARRER. *Naturwissenschaften* 9, 399-403 (1921); cf. (*C. A.* 15, 2629-31; 16, 63).—A summary of earlier work. By acid hydrolysis of heptamethylmethylcellulose, tetramethylglucose (I), and trimethylglucose (II), are obtained,



whereby the formula for cellobiose must be (III). The analogies in the behavior of starch and  $\alpha$ -amylose extend to their reactions with alk.-earth hydroxides.  $\alpha$ -Octa-amylose gives a ppt. with  $\text{Ba}(\text{OH})_2$ . A similar compd. is obtained with  $\alpha$ -tetraamylose and may be pptd. by addn. of a little  $\text{EtOH}$ .  $\alpha$ -Tetraamylose by distn. in a vacuum gives a good yield of  $\beta$ -glucosan. The formula for starch should be



The position of the anhydride bridge is undetd.

J. C. S.

The preparation of inulin, with special reference to artichoke tubers as a source. J. J. WILLAMAN. *J. Biol. Chem.* **51**, 275-83 (1922).—Grind the washed tubers as fine as possible and put into  $H_2O$  contg.  $CaCl_2$  using 1,300 cc. of  $H_2O$  and 80 g. of  $CaCl_2$  per kg. of tubers. Boil 15-20 min., ext. the juice with a press, reboil with 1 l. of  $H_2O$  and 10 g. of  $CaCl_2$ , ext. and combine the exts. Clarify with  $(AcO)_2Pb$ , avoiding a large excess, centrifuge or filter, remove the  $Pb$  with  $(NH_4)_2C_2O_4$  and centrifuge again. Treat with decolorizing charcoal if necessary. Evap. *in vacuo* to a content of 40-80% solids. Allow the sirup to cool slowly, keep at 0-5° for several hrs., thoroughly stir with an equal vol. of ice water and centrifuge. Dissolve the crystals in about 3 vols. of  $H_2O$ , filter hot, conc. to about twice the vol. of the original crystals and allow to cryst. as before in the cold. Stir with ice water, filter on paper or silk bolting cloth with suction, keeping everything as cold as possible. Wash the crystals with cold  $H_2O$ , then with 20, 50, 80, and 95%  $EtOH$ , then with  $Et_2O$  and dry at 100°. The sp. rotation of the prepn. should be at least  $-33^\circ$ . A 3rd crystn. may be made but it is useless to attempt to obtain a higher rotation than  $-39^\circ$ . The Jerusalem artichoke (girasole) tubers are not a satisfactory material for the prepn. of true inulin but are admirably adapted for investigation of the whole group of inulin substances. Dean's hypothesis that inulin is a group of substances with large, loosely bound mols., and not a single substance, is supported by the evidence obtained in the present investigation.

A. P. LOTHEROP

Structure of cellobiose. M. BERGMANN. *Naturwissenschaften* 9, 308-9(1921); cf. C. A. 15, 2420.—Cellobial, which is structurally identical with glucal, has in the reducing

half of the mol. a double linking between C atoms 1 and 2 and an "O bridge" between 1 and 4; the HO group in position 3 is not substituted. Since the C atom 6 does not take part in the formation of a disaccharide, and since in the formation of cellobial from cellobiose displacement of the glucosidic attachment does not occur, the formula for cellobiose must be  $\text{HOCH}_2\text{CH}(\text{OC}_6\text{H}_{11}\text{O}_5)\text{CH}.\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{O}$ .

J. C. S.

**Synthesis of the humic acids.** WILHELM ELLER. *Brennstoff Chem.* 3, 49-52 (1922); cf. *C. A.* 15, 83, 2850.—Arguments for the view that humic acids are aromatic in character, combining the properties of a phenol and a quinone. W. B. V.

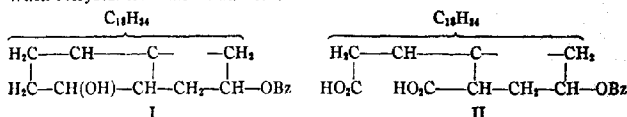
**Natural and artificial humins.** K. G. JONAS. *Brennstoff Chem.* 3, 52-5 (1922); cf. preceding abst.—Polemical. Eller's identification of natural with his artificial humic acids is premature. W. B. V.

**Synthesis of the humic acids.** WILHELM ELLER. *Brennstoff Chem.* 3, 55-6 (1922); cf. preceding abst.—Polemical in answer to Jonas. W. B. V.

**Some new color reactions of cholesterol.** LOUIS KAHLBERG. *J. Biol. Chem.* 52, 217-25 (1922).—Cholesterol, ischolesterol, phytosterol and lanolin dissolve in anhyd.  $\text{PCl}_5$ ,  $\text{POCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{SiBr}_4$  and  $\text{CBr}_4$  without color. Colored solns. are obtained in  $\text{SOCl}_2$ ,  $\text{TiCl}_4$ ,  $\text{SeOCl}_2$ ,  $\text{SbCl}_3$  and  $\text{AsBr}_3$ , but none of these reactions is sufficiently characteristic to distinguish between the different substances dissolved. Brain or gall-stone cholesterol dissolves in  $\text{AsCl}_3$  with a pink color which gradually turns a bright cherry-red on standing, more rapidly on heating. Isocholesterol gives a Co-blue soln. changing to violet, then to purple, dark red and dark green on standing, more rapidly on heating. Phytosterol yields a colorless soln. The colors of all these solns. are discharged by adding  $\text{C}_6\text{H}_6$ ,  $\text{C}_7\text{H}_8$  or  $\text{CHCl}_3$ . Concd. aq.  $\text{AsCl}_3$  (in the presence of a large excess of  $\text{HCl}$ ) gives the color reactions with cholesterol and ischolesterol on boiling. On standing the colored layers, which sep. out on the bottom of the test-tubes, are gradually hydrolyzed and become colorless as the sterol seps. out. The best reaction is obtained when anhydrous  $\text{AsCl}_3$  is used. Cholesterol seps. out practically quant. from the concd. colored solns. in  $\text{AsCl}_3$  on standing at sufficiently low temps. ( $-10^\circ$ ).  $\text{AsCl}_3$  also gives characteristic color reactions with certain other org. compds., notably those of the terpene series or derivs. thereof, a fact which supports the view that cholesterol is a terpene deriv. Further investigation in this direction is in progress. A. P. L.

**The action of benzoyl peroxide upon cholesterol.** A. WINDAUS AND H. LÜDERS. *Z. physiol. Chem.* 115, 257-69 (1921).—The work of Lifschütz (*C. A.* 14, 931) concerning an isomer of cholesterol obtained by the action of  $\text{Bz}_2\text{O}_2$  upon cholesterol was repeated and divergent results were observed. 100 g. cholesterol and 100 g.  $\text{Bz}_2\text{O}_2$  in 500 cc. 90% alc. were heated 1 hr. under a reflux condenser; thereupon 50 g. KOH in a little water was added and heating continued for one hour. The alk. mixt. was treated with an equal vol. of  $\text{H}_2\text{O}$  and then extd. with  $\text{Et}_2\text{O}$ . The washed  $\text{Et}_2\text{O}$  ext. on evapn. gave a resinous mass, which was crystd. from MeOH and recrystd. from EtOH. On purification the substance m.  $106-10^\circ$ . Yield 50%. The mother liquor gave crystals m.  $138-9^\circ$ , which proved to be unchanged cholesterol. The material m.  $106-10^\circ$  on treating with  $\text{Ac}_2\text{O}$  gave cholesteryl acetate. Yield 50%.  $\text{BzCl}$  and pyridine gave cholesteryl benzoate and a substance m.  $212^\circ$ . The cholesterol was pptd. with digitonin and the mother liquor was concd. and extd. with  $\text{Et}_2\text{O}$ . This ext. on evapn. and soln. of the residue in hot EtOH gave crystals which on washing with petroleum ether and repeated crystn. from MeOH or EtOH m.  $186^\circ$ . The compd. is cholestandiol 7-monobenzoate (I). By heating this substance with  $\text{Ac}_2\text{O}$  cholestandiol 4-acetate 7-benzoate, m.  $154^\circ$ , is obtained. The dibenzoate, m.  $211-2^\circ$ , is prepd. by dissolving the monobenzoate in pyridine, adding  $\text{BzCl}$  slowly and allowing the mixt. to stand for 24 hrs. On adding water an oily mass forms, which crysts. from alc. This compd.

in AcOH is oxidized by  $\text{CrO}_3$  to cholestan-4-one-7-ol benzoate, m.  $187^\circ$ , and the acid (II) m.  $270^\circ$ . Cholestandiol acetate was prepd. by heating cholestandiol with  $\text{Ac}_2\text{O}$ . When recrystd. from alc. it m.  $107^\circ$ .



R. L. STEHLÉ

The isomers resulting from substitutions in the cymene radical. F. W. KLINGSTEDT. *Hyllningskrift tillaghad Ossian Aschan*. 1920, 134-40.—A rept. of exptl. work which confirms the results of Bogert and Tuttle (*C. A.* 10, 2220). C. E. C.

Experiments with trifluorotoluene. FRÉD SWARTS. *Bull. acad. roy. Belg.* 1920, 389-98; cf. *Bull. acad. roy. Belg.* [iii] 35, 375-420.—By heating  $\text{PhCF}_3$  with 4 times the quantity of HBr acid (d. 1.79) in the presence of amorphous silica,  $\text{BzOH}$  is obtained quant. by the following stages:  $\text{CPhF}_2 + \text{HBr} = \text{CPhBrF}_2 + \text{HF}$ ;  $\text{CPhBrF}_2 + 2\text{H}_2\text{O} = \text{BzOH} + \text{HBr} + 2\text{HF}$ . In the presence of Fe or Cu, the side group is not attacked even at  $350^\circ$ . By nitration at  $0^\circ$ ,  $\omega$ -trifluoro-*m*-nitrotoluene is obtained,  $b_{10}$   $102-03^\circ$ , together with traces of the other isomerides. These may be isolated by transformation into the trifluorotoluidides, the Ac compds. of which are easily sepd. by fractional crystn. *m*-Acetotrifluorotoluidide m.  $103.5^\circ$ . The results obtained with the nitration of  $\text{PhCF}_3$  are in disagreement with the contention of Hollemann ("Substituierung im Benzolkern," p. 479) that the orientation of a radical is not altered when one of the elements in it is replaced by a substituent of similar behavior to the radical. J. C. S.

Catalytic hydrogenation of organic fluorine derivatives. FRÉD SWARTS. *Bull. acad. roy. Belg.* 1920, 399-417.—The catalytic hydrogenation of org. F derivs. by mol. H and Pt black proceeds differently according as the F is substituted in an aromatic nucleus or in a side chain. F derivs. of the cyclohexane series may be prepd. without attacking the side chain. The reduction of *p*- $\text{FC}_6\text{H}_4\text{CO}_2\text{H}$  in the aq. soln. of its Na salt proceeds in two well defined stages,  $\text{BzOH}$  being formed at first and cyclohexanecarboxylic acid more slowly afterwards. In the hydrogenation of  $\text{PhF}$ , the two stages are not so well defined.  $\text{SiF}_4$  and  $\text{HF}$  have no effect on the activity of the catalyst. The hydrogenation of  $\text{CPhF}_2$  (see preceding abstr.) gives exclusively *trifluoromethylcyclohexane*, a colorless liquid of unpleasant odor,  $d_{15}$  1.0870,  $d_{11.5}$  1.09800,  $b_{10.7}$   $107.05^\circ$ , liquid at  $-78^\circ$ ,  $n_D$  1.37661 (at  $11.5^\circ$ ),  $n_D$  1.37945,  $n_D$  1.38379,  $n_D$  1.38704.  $\text{PhCHF}_2$  gives by hydrogenation *difluoromethylcyclohexane*, a colorless liquid similar to the preceding compd., which  $b_{10}$   $125.25^\circ$ ,  $d_{17.5}$  1.01675. A little methylcyclohexane is also formed. The  $-\text{CHF}_2$  group is thus slowly reduced and shows less stability than the  $-\text{CF}_3$  group, a result that was expected from thermochem. considerations.  $\omega$ -*Difluorochlorotoluene* gives on hydrogenation  $\text{PhCHF}_2$ ,  $\text{PhMe}$ , and methylcyclohexane. It is not known whether  $\text{PhMe}$  and methylcyclohexane are formed from  $\text{PhCHF}_2$  in the reaction. The presence of Cl in the side group renders the F less stable and  $\text{PhMe}$  may be formed by direct reduction. More  $\text{SiF}_4$  is formed in the reduction of  $\text{PhCClF}_2$  than in the case of difluorotoluene. The hydrogenation of  $\text{F}_2\text{CHCH}_2\text{OH}$  gave no positive result. J. C. S.

Electrochemical oxidation of dimethylanilines. FR. FICHTER and EML. ROTHENBERGER. *Helvetica Chim. Acta* 5, 166-81(1922).—(1) The oxidation of  $\text{PhNMe}_2$  on a  $\text{PbO}_2$  anode in a slight excess of  $2\text{N H}_2\text{SO}_4$  (0.007-0.009 amp./cm.<sup>2</sup>) gave  $(\text{C}_6\text{H}_4\text{NMe}_2)_2$  (A). The electrolyzed soln. turned dark brown at the beginning, then gradually green and finally blue. By longer electrolysis it again became dark green. For each mol. of base 2 faradays were used. A was isolated by treating with  $\text{SO}_2$  to reduce

colored substances, boiling and pptg. with  $\text{NH}_3$ . The ppt. was dissolved in  $\text{EtOH}$ , purified with  $\text{C}$  and recrystd. from  $\text{AmOH}$ . A m.  $196^\circ$ . There were formed at the same time  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{N}_2$ , the presence of which indicated a deep-seated decompn. by oxidation, and  $\text{CH}_3(\text{C}_6\text{H}_4\text{NMe}_2)_2$ , m.  $86-7^\circ$ . The oxidation of  $\text{PhNEt}_2$  to  $(\text{C}_6\text{H}_4\text{NEt}_2)_2$  ran much more smoothly and without formation of by-products. (2) If Pt anodes were used, the oxidation ran slightly differently. By using a current strength of 1.5 amp. and a current density of 0.02 amp./cm.<sup>2</sup> on 3 moles of  $\text{H}_2\text{SO}_4$  with 1 mole of base, at  $10^\circ$ , the main product of the reaction was A but there was formed also trimethylphenyl-*p*-phenylenediamine (B). The yield of A depended on the time of electrolysis, in general increasing with the longer time. The two reaction products were isolated by pptg. the reaction mixt. with a slight excess of  $\text{Ba}(\text{OH})_2$ , filtering, pptg. the excess of  $\text{Ba}(\text{OH})_2$  with  $\text{CO}_2$ , evapg. the filtrate *in vacuo*, using  $\text{CO}_2$ , taking up the residue in  $\text{EtOH}$ , allowing to stand several days to prevent explosion during distn. and then distg. B, b.p.  $190-200^\circ$ , m.  $57^\circ$  after crystn. from  $\text{Et}_2\text{O}$ , gave a blue color with  $\text{FeCl}_3$  or other oxidizing reagents in  $\text{EtOH}$  or in aq. acid solns. Trimethylphenyl-*p*-phenylenediamine perchlorate formed light blue plates, m.  $186-7^\circ$ ; methiodide, plates from  $\text{H}_2\text{O}$ , m.  $202^\circ$ , decompd. on distn. into MeI and A, was made by the action on A of  $\text{Me}_2\text{SO}_4$  and  $\text{K}_2\text{CO}_3$  soln., acidification with  $\text{HOAc}$  and addition of KI; nitrosotrimethylphenyl-*p*-phenylenediamine, green needles from  $\text{Et}_2\text{O}$ , m.  $147-9^\circ$ , was produced by the action of  $\text{HNO}_3$  on A at  $-10^\circ$ . Two picrates from the reaction mixt. were produced, one amorphous, m.  $56-60^\circ$ , and the dimethylaniline oxide picrate, m.  $135-7^\circ$ . A trace of B was synthesized by treating dimethylphenyl-*p*-phenylenediamine with MeI to give an addition product, m.  $198-9^\circ$ . This on distn. *in vacuo* with soda lime gave B. A discussion of a possible mechanism for the formation of A and B is given. R. A.

**Action of suluryl chloride on aromatic amines.** W. FILLER AND L. KLEMM. *Ber. 55B*, 217-24 (1922).—From  $\text{PhNH}_2$  and  $\text{SO}_2\text{Cl}_2$  Wenghöfer (*J. prakt. Chem.* **16**, 451 (1877)) obtained 14-5% 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2\text{NH}_2$  (A) and a  $\text{H}_2\text{O}$ -sol. product supposed to be  $\text{PhNH}_2 \cdot \text{HCl}$ . A repetition of his work showed that there are really formed about equal amts. of A, *p*- $\text{ClC}_6\text{H}_4\text{NH}_2 \cdot \text{HCl}$  (B) and 2,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{NH}_2 \cdot \text{HCl}$  (C), with only traces of  $\text{PhNH}_2 \cdot \text{HCl}$ . The amt. of A cannot be increased at the expense of that of B and C even with a large excess of  $\text{SO}_2\text{Cl}_2$ , for the  $\text{ClC}_6\text{H}_4\text{NH}_2$  and  $\text{Cl}_2\text{C}_6\text{H}_3\text{NH}_2$  are converted as rapidly as they are formed into B and C, which do not react with  $\text{SO}_2\text{Cl}_2$  at room temp., but at higher temps. they do undergo further chlorination and pure A can be obtained almost quant. from  $\text{PhNH}_2 \cdot \text{HCl}$  and  $\text{SO}_2\text{Cl}_2$ . More than 3 Cl atoms cannot be introduced into the nucleus. Anthranilic acid gives only a mono- and a di-Cl deriv., the latter being 3,5,2- $\text{Cl}_3(\text{H}_2\text{N})\text{C}_6\text{H}_2\text{CO}_2\text{H}$  (D), while the former, m.  $204^\circ$ , is 5-chloro-2-aminobenzoic acid (E), as shown by the fact that by the Sandmeyer method it can be converted into 2,5- $\text{Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$  and by elimination of  $\text{CO}_2$  into *p*- $\text{ClC}_6\text{H}_4\text{NH}_2$ . Of the 4 possible chloro-2-aminobenzoic acids listed in Beilstein and in Richter's *Lexikon*, the 4-, 5- and 6-Cl derivs. are described as m.  $235^\circ$ ,  $148^\circ$  and  $146-7^\circ$ , while the 4th, which can be only 3-chloro-2-aminobenzoic acid (F), is given as m.  $204^\circ$ , and is therefore really E, and it is the acid m.  $148^\circ$  which is F. The error probably arose from the fact that the  $148^\circ$  acid is also designated as *m*-chloro-*o*-benzoic acid, a name which applies equally well to 5,2- and 3,2- $\text{Cl}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{CO}_2\text{H}$ . At a high temp., *o*- $\text{HO}_2\text{CC}_6\text{H}_4\text{NH}_2 \cdot \text{HCl}$  and  $\text{SO}_2\text{Cl}_2$  give D exclusively. With *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{OH}$  not only all the free positions in the nucleus but the H atoms on the N also are substituted, the product being 1-hydroxy-2,3,5,6-tetrachloro-4-dichloroaminobenzene (G), together with a small amt. of chloranil. A, m.  $77.5^\circ$ , b.  $262^\circ$ , is obtained in 70-5% yield from 45 g.  $\text{SO}_2\text{Cl}_2$  in 100 cc. ice-cold  $\text{C}_6\text{H}_6$  slowly treated with 10 g.  $\text{PhNH}_2$  in 10 g.  $\text{C}_6\text{H}_6$ , slowly heated to  $70^\circ$  and kept at that temp. until the evolution of gas ceases, and in 90-5% yield from 10 g. finely powdered  $\text{PhNH}_2 \cdot \text{HCl}$  moistened with  $\text{C}_6\text{H}_6$  treated with 34 g.  $\text{SO}_2\text{Cl}_2$  and heated 5-6



hrs. at 70° at the highest. Anthranilic acid (20 g.) introduced in the course of 10 min. into 26 g.  $\text{SO}_2\text{Cl}_2$  in 350 cc. ice-cold  $\text{Et}_2\text{O}$  yields 3 g. D and 50% E, fine needles from  $\text{EtOH}$ - $\text{H}_2\text{O}$ , m. 204° (decompn.), sol. in  $\text{H}_2\text{O}$  with faint brown color and strong violet fluorescence. D is obtained in 80-5% yield from 5 g.  $\text{HO}_2\text{CC}_6\text{H}_4\text{NH}_2 \cdot \text{HCl}$  and 10 cc.  $\text{C}_6\text{H}_6$  heated 5-6 hrs. at 65-70° with 12 g.  $\text{SO}_2\text{Cl}_2$ . G, from  $p\text{-H}_2\text{NC}_6\text{H}_4\text{OH}$  and 10 mols.  $\text{SO}_2\text{Cl}_2$  heated about 5 hrs. at 70°, m. 71.5°, can be distd. almost without decompn. with steam, is easily sol. in all org. solvents, dissolves in  $\text{AcOH}$  with brown-red color, the solu. becoming turbid on standing and depositing a ppt. which is also produced by dilg. with  $\text{H}_2\text{O}$ ; G is insol. in  $\text{H}_2\text{O}$  and dil. acids; in  $\text{NaOH}$  it dissolves slowly with violet color and on rapid acidification it can be recovered almost unchanged; long standing in alkali produces, among other changes, a liberation of  $\text{Cl}$  and  $\text{HOCl}$  can be detected by titration with  $\text{I}$ .

C. A. R.

**Rearrangement of hydrazo compounds.** PAUL JACOBSON. *Ann.* 427, 142-221 (1922); cf. *C. A.* 4, 44, 759.—*A. Rearrangement of di-p-substituted hydrazo compounds.*—While there are 2 possible isomers which may be formed by the rearrangement of the di-p-compds., when R and R' are different, only 1 o-semidine could be isolated. The difficulty of sepn. and the possible small amt. of the other isomer may account for this. The most powerful directing groups in this connection are  $\text{EtO}$  and  $\text{Me}$ . In the case of compds. containing the  $\text{AcO}$  group, there is either hydrolysis or complete removal of the group. 4-Methyl-4'-iodoazobenzene, by the action of  $\text{KI}$  upon  $\text{MeC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{N}_2\text{Cl}$ , reddish yellow, glistening leaflets, m. 165-6°.  $\text{H}_2\text{S}$  in  $\text{NH}_4\text{OH}$  reduces it to the hydrazobenzene, needles, m. 134°. The rearrangement was carried out by heating 10 g. with 12 g.  $\text{SnCl}_4$  and 30 cc. 25 %  $\text{HCl}$ . 5-Methyl-4'-iodo-2-aminodiphenylamine (A) is formed in about 40% yield, m. 116-7°. Salicylaldehyde derivative, yellow needles, m. 132-4°. 6-Methyl-1-[p-iodophenyl]-2-mercaptobenzimidazole, by heating A in 10 parts  $\text{EtOH}$  with 5 parts  $\text{CS}_2$ , fine needles, m. 284-5°. Sodium salt, *Mercury salt*, needles. Methyl ether, needles, m. 139-40°. For purposes of comparison, 4'-methyl-5-iodo-2-nitrodiphenylamine (from  $p\text{-MeC}_6\text{H}_4\text{NH}_2$  and  $3,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{I}$ ), red, felt-like needles, m. 104° was reduced to the 2-amino derivative, leaflets, m. 86-7°, which gives a red-violet turbidity with  $\text{FeCl}_3$  and a salicylaldehyde derivative, yellow needles, m. 148°. That the rearrangement product of  $\text{MeOC}_6\text{H}_4\text{NHNHC}_6\text{H}_4\text{OEt}$  is 4'-methyl-5-ethoxy-2-aminodiphenylamine (*Ann.* 287, 177 (1895)) is proven by its synthesis from 4'-methyl-5-ethoxy-2-nitrodiphenylamine (long, light brown needles, m. 104°) by reduction with alc.  $(\text{NH}_4)_2\text{S}$  in a sealed tube, and the m. p. of the salicylaldehyde derivative, yellow needles, m. 121-4°. 4-Bromo-4'-ethoxyazobenzene, from  $\text{EtONa}$  and  $\text{EtI}$  acting on  $\text{BrC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{OH}$ , yellow, glistening needles, m. 135-6°. With  $\text{Zn}$  dust and  $\text{NaOH}$  in alc., the hydrazobenzene is formed, needles which soon turn yellow in the dark, m. 81-3°. Rearranged by treating with  $\text{ZnCl}_2$  and  $\text{HCl}$  in alc., 4'-bromo-5-ethoxy-2-aminodiphenylamine (B) is formed in a yield of about 48%, needles, m. 67-8°. It was characterized by the following derivs. 1-[p-Bromophenyl]-6-ethoxybenzotriazole, by the action of  $\text{C}_6\text{H}_5\text{NO}_2$ , long, pointed leaflets, m. 145-6°.  $\text{HCO}_2\text{H}$  gives the benzimidazole, needles, which turn violet in the air, m. 120° and form a colorless formate. Heated with 10 parts 25 %  $\text{H}_2\text{SO}_4$  in a sealed tube at 180°, 1-[p-bromophenyl]-6-hydroxybenzimidazole results, pale violet needles, m. 295°. 1-[p-Bromophenyl]-6-ethoxy-2-mercaptobenzimidazole, pointed needles, m. 255°. Salicylaldehyde derivative, small, yellow needles, m. 151°. 5-Bromo-4'-ethoxy-2-nitrodiphenylamine, dark red needles, m. 115°. The corresponding 2-amino derivative, isomeric with B, could not be crystd. but was characterized by the asimide, 1-[p-ethoxyphenyl]-6-bromobenzotriazole, needles, m. 129°, and the salicylaldehyde derivative, long, red-yellow needles, m. 146-7°. The rearrangement of 4-methyl-4'-acetoxyhydrazobenzene (*Ber.* 24, 2310) gives 5-methyl-4'-hydroxy-2-aminodiphenylamine, glistening needles, m. 137°, in 31 % yield; its constitution is established by de-

compn. into  $p\text{-C}_6\text{H}_4(\text{OH})_2$  and  $3,4\text{-(H}_2\text{N)}_2\text{C}_6\text{H}_2\text{Me}$ . *6-Methyl-1-[p-hydroxy]benzotriazole*, pale yellow leaflets, m.  $187.5\text{--}9.5^\circ$ ; with EtI and Na it forms an *ethoxy derivative*, plates, m.  $91^\circ$ . The *p*-semidine, which is formed in 24 % yield, is  $\text{MeC}_6\text{H}_4\text{NHC}_6\text{H}_4\text{NH}_2$  (*Ann.* 255, 166(1889)). *Salicylaldehyde derivative*, m.  $142^\circ$ .  $\text{FeCl}_3$  gives a bluish violet changing to fuchsin-red color, changed by concd. HCl to yellow. *3',4'-Dimethyl-4'-acetoxysazobenzene*, fine needles, m.  $65\text{--}6^\circ$ . The rearrangement was carried out with  $\text{ZnCl}_2$  in HCl below  $35^\circ$ , and the products sepd. by crystn. from  $\text{H}_2\text{O}$ . The *p*-semidine, 16 % yield, seps. as the HCl salt and is *2,4'-dimethyl-4'-aminodiphenylamine*, fine, glistening needles, m.  $78.5^\circ$ . The dil. HCl soln. gives a violet color with  $\text{FeCl}_3$  and a carmine-red color with  $\text{NaNO}_2$ . *Salicylaldehyde derivative*, needles, m.  $116.5^\circ$ . The *o*-semidine, *3',5'-dimethyl-4'-hydroxy-2-aminodiphenylamine* (40% yield), could not be isolated as such, but was analyzed as *1-[m-methyl-p-hydroxyphenyl]-6-methylbenzimidazole*, glistening leaflets, m.  $196\text{--}7^\circ$ . *Hydrochloride*, leaflets. *p*-*Ethoxy derivative*, analyzed as the *hydrochloride*, fine, long, rhombic needles, and as the *picrate*, flat prisms, m.  $186\text{--}7^\circ$ . *4,4'-Dimethyl-5-ethoxy-2-aminodiphenylamine* (*Ann.* 287, 201), m.  $80\text{--}90^\circ$ ; the *methylene deriv.*, *5-methyl-1-[p-tolyl]-6-ethoxybenzimidazole*, forms fine needles, m.  $102.5^\circ$ , and gives a *picrate*, needles, m.  $228^\circ$ . In the rearrangement of  $\text{BrC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{OAc}$  (*Ber.* 31, 2116) only 5 % of *4'-bromo-4'-aminodiphenylamine* is obtained, compact needles, m.  $93.5^\circ$ .  $\text{FeCl}_3$  gives a blue-violet color, changing to brick-red.  $\text{NaNO}_2$  gives a dark red color changing through orange to light yellow. *Salicylaldehyde derivative*, yellow leaflets, m.  $172^\circ$ . *4-Ethoxy-4'-dimethylaminoazobenzene*, brown, glistening, 4-sided plates, m.  $149\text{--}50^\circ$ , the *hydrochloride* of which forms a lustrous, blue, felt-like crystal mass. Rearrangement gave *5-ethoxy-4'-dimethylamino-2-aminodiphenylamine* (C), oily. *Salicylaldehyde derivative*, golden leaflets with metallic reflex, m.  $141.5\text{--}2.5^\circ$ . *1-[p-Dimethylaminophenyl]-2-[o-hydroxyphenyl]-6-ethoxybenzimidazole*, glistening needles, m.  $182\text{--}3^\circ$ , not hydrolyzed by acids. *1-[p-Dimethylaminophenyl]-6-ethoxybenzimidazole*, needles after purifying through the *picrate* (green-yellow needles), m.  $141\text{--}3^\circ$ , forming a double salt with  $\text{HgCl}_2$ . *2,3-Diphenyl-1-[p-dimethylaminophenyl]-2-hydroxy-7-ethoxyquinoxaline-1,2-dihydrate*, by condensation with benzil, fine, canary-yellow needles, m.  $187\text{--}90^\circ$ . *5-Chloro-4'-dimethylamino-2-nitrodiphenylamine*, from  $1,3,4\text{-(O}_2\text{N)}_3\text{C}_6\text{H}_2\text{Cl}$  and  $\text{H}_2\text{NC}_6\text{H}_4\text{NMe}_2$ , reddish brown needles, m.  $181^\circ$ . With  $\text{EtONa}$ , the *5-ethoxy-derivative* results, dark brown, pointed crystals, m.  $122\text{--}3^\circ$ , which is reduced to C by  $\text{SnCl}_2\text{--HCl}$ , and identified by the above derivs. Trials with  $\text{H}_2\text{NC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{NMe}_2$ ,  $\text{AcNHC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{NMe}_2$ , and  $\text{Me}_2\text{NC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{NMe}_2$  gave only decompn. products. The rearrangement of  $\beta,\beta'$ -hydrazonaphthalene to *2,2'-diamino-1,1'-dinaphthyl* (*Ber.* 36, 4154) has been confirmed; the *salicylaldehyde derivative* (*2,2'-bis-[p-methoxybenzylidene-amino]-1,1'-dinaphthyl*), yellow powder, m.  $194\text{--}5^\circ$ . B. Rearrangement of simple *p*-substituted hydrazo compounds.—*Methyl 4-methoxyazobenzene-3-carboxylate*, m.  $65\text{--}7^\circ$ . The free acid forms small, red needles, m.  $167^\circ$ , and upon reduction with Sn and HCl in MeOH forms  $5,2\text{-MeO(H}_2\text{N)}_2\text{C}_6\text{H}_2\text{NHPH}$  (*Ber.* 29, 2681), the yield being less than 10 %.  $2,3,4\text{-Me}_3(\text{AcNH})\text{C}_6\text{H}_2\text{N}_2\text{Ph}$ , upon reduction with  $\text{ZnCl}_2$  gives *3,3'-dimethyl-4'-amino-4'-acetaminodiphenylamine*, m.  $174\text{--}5^\circ$ . The HCl soln. gives a red-violet color with  $\text{FeCl}_3$  or  $\text{NaNO}_2$ . The *salicylaldehyde derivative*, yellow needles, m.  $185\text{--}6^\circ$ . The principal product of the rearrangement, however, is *3',4'-dimethyl-2,4'-diamino-5-acetaminodiphenyl*, characterized by its *benzaldehyde derivative* (*3',4'-dimethyl-2,4'-bis-[benzylideneamino]-5-acetaminodiphenyl*), yellowish white, m.  $204\text{--}5^\circ$ ; the *salicylaldehyde derivative*, pale yellow needles, m.  $239\text{--}40^\circ$ , and the *acetyl derivative*, clear plates, do not m.  $380^\circ$ . C. Rearrangement of non-*p*-substituted hydrazo compounds.—In studying the rearrangement of di-*m*-substituted derivs., *3,5-dimethylazobenzene*, prepd. from PhNO and *m*- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$ ,  $b_{17\text{--}19}$   $197.5^\circ$ , was used. On reduction, this gave the *hydrazobenzene*, long, fine needles, m.  $78\text{--}9^\circ$ . The product of the action of  $\text{ZnCl}_2$  and HCl

in EtOH is *2,6-dimethyl-4,4'-diaminodiphenyl (2,6-dimethylbensidine)*, long needles, m. 124°. *Benzaldehyde derivative*, pale yellow, hair-like needles, m. 199-200°. Deamination gives *2,6-dimethyldiphenyl*, b. 260-5°, which was also synthesized from *m*-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> through the diazo compd. and C<sub>6</sub>H<sub>6</sub>. Nitrated at room temp. a *trinitro derivative* is formed, transparent, 4-sided plates, m. 257-8°, while warming 3 hrs. gave a *tetranitro derivative*, rectangular microplates, m. 227-9°. *2,4-Dimethyldiphenyl*, from 2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>, b<sub>105</sub> 270-6°, and giving a *tetranitro derivative*, m. 154-5°. Finally, attempts were made to det. whether hydrazones containing aromatic and aliphatic groups, or those of the type (PhCH<sub>2</sub>NH)<sub>2</sub> would behave as above. *Pyroracemic aldehyde p-ethoxyphenylhydrazone*, orange-yellow leaflets, m. 144.5°. A by-product in the reaction is *di-p-ethoxyformazyl methyl ketone*, glistening, red needles, m. 143°, sepd. by its insoly. in alc. *Pyroracemic acid p-ethoxyphenylhydrazone*, canary-yellow needles, m. 120-2° (decompn.). *Ethyl ester*, red needles, m. 110°. The reduction of the Na salt with Na-Hg gives  $\alpha$ -[*p*-ethoxyphenylhydrazino]propionic acid, fine, yellowish white needles, m. 128-38° (decompn.), and reduces cold Fehling soln. Other expts. in this direction were without results. Full exptl. details of the above work are found in dissertations covering the period of 1894-1909.

C. J. WAST

**Summary of the results of the rearrangement of hydrazo compounds, with a consideration of their importance.** PAUL JACOBSON. *Ann.* 428, 76-121(1922); cf. preceding abstr.—A collective article which lists all the possible transformations of hydrazo compds., gives references to the literature for all recorded rearrangements, states the rules regarding the influence of substituents and discusses the mechanism of the rearrangement.

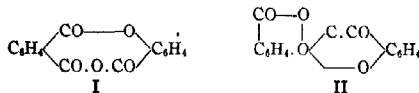
C. J. WAST

**The melting points of some aliphatic aromatic ketones.** RIKO MAJIMA, KWANTO NAGAOKA and KEISUKE YAMADA. *Ber.* 55B, 215-7(1922); cf. *C. A.* 8, 934.—The observation previously made by various investigators that in a homologous series the m. ps. of compds. with an even no. of C atoms are in general higher than those of the next lower and higher homologs with an uneven no. of C atoms has been found to hold good for aliphatic aromatic ketones as regards the no. of C atoms in the side chain, as shown by the following m. ps. of the 3 series of compds. 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COR, *p*-MeOC<sub>6</sub>H<sub>4</sub>COR and PhCOR, resp.: R = C<sub>10</sub>H<sub>21</sub>, —, 49, —; C<sub>11</sub>H<sub>23</sub>, 68-9, 62.5, 45; C<sub>12</sub>H<sub>25</sub>, 59.5-60.0, 59, 41-2; C<sub>13</sub>H<sub>27</sub>, 74-5, 67, 54-5; C<sub>14</sub>H<sub>29</sub>, 64-5, 65-6, 50-1; C<sub>15</sub>H<sub>31</sub>, 79-80, 72-3, 59-60; C<sub>16</sub>H<sub>33</sub>, 67-8, 70.5, 56-6.5; C<sub>17</sub>H<sub>35</sub>, 82-3, 77-7.5, —. C. A. R.

**Electrolytic reduction of some carboxylic acids.** HARUSHIGE INOUE. *J. Chem. Ind. (Japan)* 24, 906-18(1921).—(1) PhCH<sub>2</sub>CO<sub>2</sub>H.—With a cathodic soln. consisting of 20 g. PhCH<sub>2</sub>CO<sub>2</sub>H, 70 g. 75% H<sub>2</sub>SO<sub>4</sub>, 60 g. 96% alc. and an anodic soln. of 20-30% H<sub>2</sub>SO<sub>4</sub>, using a Pb plate covered with PbO<sub>2</sub> as cathode, a current d. of 10 amp./dm.<sup>2</sup> (40 amp. hrs. in all), and with 5 v. of mean p. d., at 60° (cathodic soln.), I. obtained 53.45% of PhCH<sub>2</sub>CH<sub>2</sub>OH. At the end of reduction, the electrolyte is extd. with ether. The ether ext. is fractionated into 2 parts by steam distn. The volatile part consists of PhCH<sub>2</sub>CH<sub>2</sub>OH, PhCH<sub>2</sub>CO<sub>2</sub>Et, and PhCOEt. By sapon., pure PhCH<sub>2</sub>CH<sub>2</sub>OH is obtained. From the non-volatile fraction, a compd. m. 114.5° is obtained, which is proved to be [PhCH<sub>2</sub>CH(OH)]<sub>2</sub>, optically inactive, sol. in alc., and less sol. in ether. In order to avoid production of PhCH<sub>2</sub>CH<sub>2</sub>OH as the ester, I. used the same method in acetone soln. The product, however, has an acetone odor and is not fit for use in perfumery. By this method, however, I. isolated from the ether-insol. fraction white crystals, m. 145°, of PhCH<sub>2</sub>CH(OH)C(OH)Me<sub>2</sub>. (2) Cinnamic acid.—By a similar method of reduction, I. obtained 38.46% of PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH from PhCH=CHCO<sub>2</sub>H. From the ether-insol. fraction, [PhCH<sub>2</sub>CH<sub>2</sub>CH(OH)]<sub>2</sub> m. 108-9° was obtained. (3) BzOH.—78% of BzOH can be reduced to PhCH<sub>2</sub>OH by the same method.

S. T.

**Substituted salicylic acids.** I. H. P. KAUFMANN AND W. KAUFMANN. *Ber.* 55B, 282-8(1922).—In the course of an investigation on the influence of different substituents on the physiol. properties of salicylic acid (A) a no. of interesting chem. observations was made.  $\text{AcOCH}_2\text{COCl}$  (20 g.) and 25 g. dry  $\text{HOC}_6\text{H}_4\text{CO}_2\text{Na}$  in  $\text{C}_6\text{H}_6$  allowed to stand 3 days in a desiccator yield about 13 g. *acetylglucosylsalicylic acid*, needles from  $\text{C}_6\text{H}_6$ , easily decomp. in the air, m.  $103-4^\circ$ , difficultly sol. in  $\text{H}_2\text{O}$ , which on moderate warming hydrolyzes it to A and  $\text{AcOCH}_2\text{CO}_2\text{H}$ . From 10 g. *o*- $\text{C}_6\text{H}_4(\text{COCl})_2$ , m.  $268^\circ$ , and 14 g.  $\text{HOC}_6\text{H}_4\text{CO}_2\text{Na}$  boiled 8 hrs. in dry  $\text{C}_6\text{H}_6$  is obtained, besides NaCl, A and unchanged  $\text{HOC}_6\text{H}_4\text{CO}_2\text{Na}$ , 8 g. of a compound (B),  $\text{C}_{11}\text{H}_8\text{O}_8$ , needles from 80% alc., m.  $158.5^\circ$ , gives no  $\text{FeCl}_3$  reaction even after long boiling with NaOH, mol. wt. in freezing  $\text{C}_6\text{H}_6$  287, also obtained in 3 g. yield from 5 g.  $\text{C}_6\text{H}_4(\text{COCl})_2$  boiled 12 hrs. in  $\text{C}_6\text{H}_6$  with 4.5 g.  $\text{NaOC}_6\text{H}_4\text{CO}_2\text{Na}$ ; 3 g. heated 8 hrs. at  $120^\circ$  in a sealed tube with 10% alc. NaOH gives 1.44 g. A and 1.88 g. *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ , while 5 g. in AcOH under a reflux treated in the course of 1 hr. with 12 g. Zn dust and boiled 10 hrs. longer gives, besides



1.5 g. unchanged B, 1.65 g. phthalide and 1.3 g. A. It must be left to further expts. to det. whether B has the structure I or II.

C. A. R.

**Crystalline form of trimethylphloretin.** MARIA DE ANGELIS. *Atti accad. Lincei* [v] 30, i, 348-51(1921).—This compd.,  $\text{C}_{24}\text{H}_{20}\text{O}_6$ ,  $\text{Me}_3\text{COCHMeC}_6\text{H}_4\text{OH}$  (cf. Ciamcian and Silber, *Ber.* 28, 1393-8(1895)), forms crystals belonging to the prismatic class of the monoclinic system,  $a : b : c = 0.4505 : 1 : 0.3410$ ,  $\beta = 71^\circ 13'$ ,  $d$  1.306.

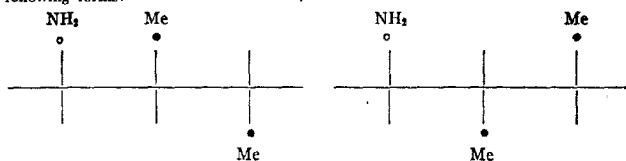
J. C. S.

**Esterification of dimethylaminoisophthalic acid.** I. Preparation of methyl 4-aminoisophthalate. N. SMODLAKA. *Rev. chim.* 1, 71-4(1921); cf. C. A. 14, 3408.—4-Acetylaminoisophthalic acid, when treated with MeOH and  $\text{H}_2\text{SO}_4$ , undergoes simultaneous de-acetylation and esterification, yielding Me 4-aminoisophthalate, m.  $131^\circ$ , along with a small quantity of an acid by-product, m.  $220^\circ$ , which, apparently is MeH 4-aminoisophthalate. The yields throughout are good (cf. Wegscheider, Malle, Ehrlich, and Skutzky, C. A. 13, 1832). II. Preparation of 4-dimethylaminoisophthalic acid. III. Esterification of 4-dimethylaminoisophthalic acid. *Ibid.* 88-101.—Me 4-aminoisophthalate is converted by means of  $\text{Me}_2\text{SO}_4$  successively into methyl 4-methylaminoisophthalate, m.  $115^\circ$ , and Me 4-dimethylaminoisophthalate, both of which yield the corresponding acids on hydrolysis with alc. KOH. The work described in paper (III) has already been published (C. A. 14, 3408).

J. C. S.

**Determination of the configuration of stereoisomeric hexamethylenes.** A. SKITA. *Ann.* 427, 256-80(1922).—2,4- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$  was purified through the acetate and reduced with colloidal Pt and H with a pressure of 3 atm. and at  $50-60^\circ$ , giving 2,4-dimethylcyclohexylamine, b.  $161-4.5^\circ$ . Benzoate, m.  $135-50^\circ$ . Crystn. from EtOH seps. the benzoate into 2 isomers. (In the following, *c* means *cis* and *t*, *trans*.) 1<sup>c</sup>-Amino-2<sup>c</sup>,4<sup>c</sup>-dimethylcyclohexane (A), from the more sol. fraction, b.  $163-4.5^\circ$ ; benzoate, needles, m.  $86^\circ$ ; acetate, m.  $29^\circ$ , b.  $149^\circ$ ; phenylurethan, m.  $60^\circ$ ; sym-thiourea, compact crystals, m.  $182^\circ$ ; picrate, thick leaflets, m.  $176-7^\circ$ ; hydrochloride, needles, m.  $223^\circ$ . 1<sup>c</sup>-Amino-2<sup>c</sup>,4<sup>c</sup>-dimethylcyclohexane, from the insol. portion, b.  $161.5-2.5^\circ$ ; benzoate, m.  $198^\circ$ ; acetate, needles, m.  $120^\circ$ ; phenylurethan, compact needles, m.  $128^\circ$ ; thiourea, fine needles, m.  $215^\circ$ ; picrate, yellow leaflets, m.  $155-6^\circ$ ; hydrochloride, needles, m.  $235^\circ$  (decompn.). The use of HCl during the reduction produces a larger amt. of the *cis*-

compd. The reduction of 2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH gave *trans*-1,3-dimethylcyclohexane, b. 119–121°, and *trans*-2,4-dimethylcyclohexane, b. 175–7°, the *phenylurethan* of which m. 96°. With CrO<sub>3</sub> in AcOH, it is oxidized to 2,4-dimethylcyclohexanone, peppermint-like oil, b. 176–7.5°; *oxime*, glistening needles, m. 95°; *semicarbazone*, leaflets, m. 190°. Upon reduction of the ketone in acid soln. A was obtained, while in alk. soln. the reaction product was *trans*-1,3-dimethylcyclohexane, the *phenylurethan* of which m. 96°. The reduction of the ketone *oxime* in HCl gave the *cis*-deriv. Smaller amts. of HCl favored the formation of the *trans*-deriv. (benzoate, m. 198°), while larger amts. decompd. the *oxime*. The reduction of the *oxime* with EtOH and Na gave the *trans*-deriv. The configuration of the two forms is represented by the following forms:



C. J. WERT

**Sulfamidophthalic acid and sulfimidophthalic acid.** TH. ZINCKE AND H. GRUNGE. *Ann.* 427, 221–55 (1922); cf. *Am. Chem. J.* 5, 106; 6, 262; 13, 193; *C. A.* 13, 574.—The following salts of saccharincarboxylic acid are described: *Acid N-potassium* (A), thick hard spears, needles or leaflets, with 1 H<sub>2</sub>O easily removed *in vacuo* at 100°; 100 parts cold H<sub>2</sub>O dissolve 0.06 part salt; on heating CO<sub>2</sub> is given off, probably forming saccharin. The *acid carboxyl potassium salt* (B) results by heating the acid K sulfamidate at 150°, cryst. powder, easily sol. in H<sub>2</sub>O. Warming with H<sub>2</sub>O changes it to the difficultly sol. *N-K salt*. *Neutral barium salt*, aggregates of needles with 2 H<sub>2</sub>O, lost at 100° *in vacuo*. *Acid N-silver salt*, from A by pptn. with AgNO<sub>3</sub>, flat, glistening needles with 1 H<sub>2</sub>O. *Acid carboxyl silver salt*, (C), amorphous powder, very slightly sol. in H<sub>2</sub>O. *Neutral silver salt*, by neutralizing the acid salt and pptg. the soln. with excess AgNO<sub>3</sub>, H<sub>2</sub>O-free powder. The esters of the sulfimide can only be obtained by the use of the salts; the free acid gives esters of the sulfamidic acid. The *N-Me ester* was prepd. from the Ag or K salt and MeI in sealed tubes, needles, m. 189°. The ester is very stable and is not transformed into a deriv. of the sulfamidic acid. *Concd. HCl* at 150° splits off MeNH<sub>2</sub>. The *carboxyl methyl ester* (D) may be prepd. from the Ag salt and MeI at 100° by heating the sulfamidic acid ester until a clear melt is obtained, or by dissolving the neutral ester in 2 N NaOH and pouring the clear soln. into excess of dil. HCl, needles, m. 184–5°, sapond. by long treatment with 2 N NaOH with formation of sulfimidophthalic acid. The *carboxyl ethyl ester* forms small needles, m. 156–7°. The *dimethyl ester*, prepd. from the neutral salt, forms glistening, easily sublimed needles, m. 176°. The dry *N-K salt* heated with 2 parts PCl<sub>5</sub> for 2 hrs. at 150° forms *pseudosulfimidophthalic acid dichloride*, needles, m. 156°. With MeOH, the *dimethyl ester* results, small tables, m. 163°. *Diethyl ester*, small plates, m. 142–3°. *Diamide*, fine needles, does not m. 280°. Salts of sulfamidophthalic acid: *acid potassium*, small needles; 100 parts H<sub>2</sub>O dissolve 5 parts at 20°. Warming with water gives A. At 150° the salt loses 1 H<sub>2</sub>O, forming B. *Barium*, cryst. powder, so insol. that it may be used as a test for the acid. *Acid silver*, amorphous powder, scarcely sol. in H<sub>2</sub>O and losing 1 mol. H<sub>2</sub>O at 150°, giving C. *Neutral silver salt*, amorphous powder. *Acid methyl ester*, from the acid and MeOH, fine, glistening needles, m. 205°. *Concd. HCl* at 150° splits off NH<sub>3</sub>. Heated above its m. p., it loses H<sub>2</sub>O, giving D. With MeOH and HCl the di-Me ester is obtained. *Diethyl ester*, glistening leaflets and needles, m. 104–5°. The sulfimidophthalic acid is

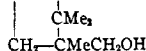
stronger than the sulfamidic acid, the cond. of the 2 acids at 25° being ( $\nu = 100$  and 200): sulfamide, 338, 350; sulfamidic, 209, 249. The cond. of the 2 esters at 25° is: carboxyl ester, 348 ( $\nu = 400$ ); *N*-ester, 258. The values of  $K$  are:  $K_{NH}$  0.03111;  $K_{COOH}$  0.0088. C. J. WEST

Constituents of resins. VIII. Amyrins from elemi resin. II.  $\alpha$ -Amyrin. ALOIS ZENKE, ALFRED FRIEDRICH, OTTO JOHANNSEN AND RUDOLF RICHTER. *Monatsh.* **42**, 439-45 (1922); cf. *C. A.* **15**, 1016, 1507.—The distn. of  $\alpha$ -amyrin benzoate in a stream of  $CO_2$  gave an amyrene,  $C_{10}H_{18}$ , isolated as the dibromide, prismatic needles, m. 259-60°. With  $CrO_3$  in AcOH  $\alpha$ -amyrin gives  $\alpha$ -amyranone (A),  $C_{10}H_{16}O$ , cubes or plates, m. 124°. The oxime m. 234°. With  $BzCl$   $\alpha$ -amyrenol benzoate is formed, fine leaflets, m. 197-8°, which gives A on sapon. Bromo- $\alpha$ -amyrin, by sapon. of the Bz deriv., fine needles with 0.5 mol.  $H_2O$ , m. 122-50°, anhydrous, m. 178-9°.  $CrO_3$  oxidizes this to bromo- $\alpha$ -amyranone, fine leaflets, m. 190°; oxime, needles, m. 236.5°; benzoate, leaflets, m. 226-7°. IX. Decomposition of d-siarsinolic acid and of lubanol benzoate. A. ZINKE, FRANZ HANSELMAYER, AND WILHELMINE EHMER. *Ibid* 447-52; cf. *C. A.* **13**, 2675.—The oxidation of d-siarsinolic acid or of l-prabangic acid leads to the formation of an acid,  $C_{21}H_{34}O_8$ , needles, m. 285-6°, which is dibasic but which does not yield a cryst. ester or oxime. The formula for lubanol benzoate receives further confirmation in the fact that a KOH melt gave 1,2,4- $C_6H_3(OH)_2CO_2H$ . Vanillin has also been prepd. from the benzoate. C. J. WEST

Preparation of glycols corresponding with pinic, norpinic, and d-camphoric acids and their derivatives. G. J. ÖSTLING. *Översikt Finska Vetenskaps Soc.* **57** [A], No. 7, 19 pp. (1914).—2, 2-Dimethyl-1,3-dimethanolcyclobutane,  $HOCH_2CH \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CMe_2 \end{smallmatrix} CHCH_2OH$

OH, is prepd. by acting on alc. di-Et norpinate with metallic Na at 140°, adding water, and heating for some hrs., distg. off the alc., and extg. the alk. soln. with ether. It is a viscous liquid of aromatic odor,  $b_D^{15}$  150-2°. The dibromide,  $C_8H_{14}Br_2$ , is a colorless liquid,  $b_D^{10}$  128-30°. 2,2-Dimethyl-1-methanol-3- $\beta$ -ethanolcyclobutane,  $HOCH_2CH \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CMe_2 \end{smallmatrix} CHCH_2CH_2OH$ , the glycol corresponding with pinic acid, prepd. similarly,

is a liquid,  $b_D^{17}$  166-7°. The dibromide,  $C_9H_{16}Br_2$ , is a liquid,  $b_D^{10}$  144-5°. Methyl camphorate, prepd. by the action of alc. camphoric acid on  $Me_2SO_4$  in the presence of KOH at the ordinary temp.,  $b_D^{13}$  133°,  $d_4^{15}$  1.0799,  $n_D^{19}$  1.46271,  $[\alpha]_D$  49.07°. This and the di-Et salt, as in the case of norpinic acid esters, give on reduction, 1,2,2-trimethyl-1,3-dimethanolcyclopentane  $CH_2-CHCH_2OH$ , forming long needles, m. 126-7°. The



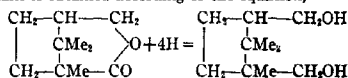
corresponding oxide,  $C_{10}H_{18}O$ , is prepd. by heating the glycol with HCl; it forms leaf-like crystals of camphor-like odor, m. 176°. By acidifying the residue obtained after removing the reduction products of Et camphorate, an oily acid is obtained which gives campholide by heating in a vacuum. This by reduction gives the glycol above described. Reduction of camphoric anhydride gives the glycol in small amts. as well as campholide and camphoric acid. J. C. S.

Formation of bicyclic systems with cyclobutane rings. G. J. ÖSTLING. *Översikt Finska Vetenskaps Soc.* **57**, [A], No. 23, 14 pp. (1915).—An attempt to prep. a bicyclic cyclobutane compd. by acting on the dibromide obtained from the glycol of pinic acid (see preceding abstr.) with Na was unsuccessful. By the action of Na on Et pinate complex products were obtained. The dry distn. of Pb pinate gave a ketone,  $C_{12}H_{20}O$ , of pleasant odor,  $b_D^{13}$  93-5°,  $d_4^{19}$  0.9448,  $n_D^{18}$  1.4755; it is probably identical with the substance obtained by the distn. of Ca pinate (Bonsdorff, *C. A.* **6**, 485). The semicarbazone

m. 160°. Dry distn. of Ca camphorate gave a good yield of camphoric anhydride.

J. C. S.

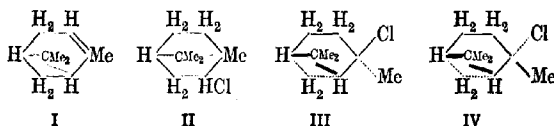
**1,2,2-Trimethyl-1,3-dimethanocyclopentane.** G. J. ÖSTLING. Z. "Technikern" 1916, Jan.—By reduction of campholide (see preceding absts.), 1,2,2-trimethyl-1,3-dimethanocyclobutane is obtained according to the equation,



Oxidation of the glycol gives *d*-camphoric acid; it has  $[\alpha]_D^{20}$  64.07° (in alc.). The inner oxide, formed by the elimination of water, gives  $[\alpha]_D^{20}$  27.20° (in ether). The corresponding dibromide was prepd., but not in a state of purity.

J. C. S.

***tert*-Pinene hydrochloride.** The pinacolin transformation. OSSIAN ASCHAN. Översikt Finska Vetenskaps Soc. 57, [A], No. 1, 35 pp. (1914).—The action of dry HCl on pinene (I) at low temps. does not give ordinary pinene hydrochloride (bornyl chloride) (II), but an isomeric liquid compd., *tert*-pinene hydrochloride (III). This compd. differs from II in that it contains the bicyclic tetrocean system of pinene and decomp. partly on treatment with  $\text{PhNH}_2$ , giving H chlorides and a pinene which is optically active in the same sense as the original material. The elimination of HCl takes place with development of heat, III being stable only below  $-10^\circ$ . In the absence of cooling, the temp. rises to 60–80° with transformation into solid II.



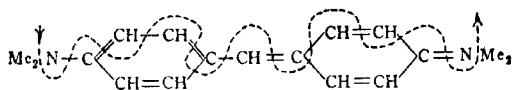
It is supposed that in the formation of II from pinene and HCl (pinacolin transformation) the unstable compd. III occurs as an intermediate product. Nopinene forms with HCl the same compd. III as is given by ordinary pinene with  $\text{PhNH}_2$ . The change from nopinene to ordinary pinene by way of the compd. III takes place more directly and simply than the change by way of nopinic acid  $\rightarrow$  nopinone  $\rightarrow$  nopinolacetic acid (Wallach, C. A. 4, 186). No verifiable amt. of nopinene is formed in the decompn. above mentioned. The compd.,  $\text{C}_{10}\text{H}_{17}\text{Cl}$ , obtained by Wallach by the action of  $\text{PCl}_5$  on methylpinol is probably a stereoisomeride of the compd. III and may have the constitution represented by formula IV. (The thick lines are supposed to be above and the dotted lines below the plane of the paper in formulas III and IV.) The rate of transformation of III is greater than its rate of formation from pinene and HCl above 0°, and even at low temps. it cannot be obtained free from II. It has a suffocating odor and attacks the mucous membrane strongly. The satn. of the original hydrocarbon with dry HCl was carried out at  $-15^\circ$  with the addn. of 4 to 10% of ether. On adding to the hydrochloride an equal vol. of  $\text{PhNH}_2$  and leaving it at the ordinary temp., the transformation sets in quickly and the temp. of the mixt. rises above 80°. When the temp. falls again the mixt. is heated for about 4 hrs. on a water-bath. Glacial  $\text{AcOH}$  is added to fix the excess of  $\text{PhNH}_2$  and volatile products are removed by steam distn. The principal product is II. The mixt. of hydrocarbons resulting from its decompn. consists essentially of ordinary pinene, but contains some dipentane and limonene. The fraction b. 162–7° appears to contain an unknown bicyclic terpene. By using pinene from different sources with varying optical rotations, different results were obtained for the yield both of II and of regenerated pinene.

J. C. S.

**Abietic acid and certain metal abietates.** L. L. STEELE. J. Am. Chem. Soc. 44,

1333-41(1922).—Abietic acid (A) can be obtained in 350 g. yield by boiling 700 g. white rosin in 500 cc. of 98% AcOH 2 hrs. under a reflux, filtering hot, cooling to room temp. and seeding; after 2 crystns. (best from 98% AcOH) it m. 161-5° and forms 3-sided tables with angles of approx. 45° and 90°,  $a(100)A\mu(1\bar{1}0) 47^{\circ}29'$ ,  $a(100)Ac(001) 68^{\circ}22'$ ,  $c(001)A(101) 48^{\circ}1'$ ,  $a(100)A\omega(1\bar{1}1) 70^{\circ}7'$ ,  $\alpha 1.510$ ,  $\beta 1.578$ ,  $\gamma 1.618$ ,  $[\alpha]_D^{25} -80.0^{\circ}$  (approx. 10 g. in 100 cc. abs. alc.), I no. (Wijs) 152.7-3.2 at 0°, 166.8-9.3 at 22-3°, 168.5-71.1 at 25-6°, acid no. (in alc. with phenolphthalein) 186. The following salts were prepd. by slowly pouring A neutralized in denatured alc. to a faint pink with alc. NaOH and phenolphthalein into 1.5 times the calcd. amt. of the appropriate metallic salt in H<sub>2</sub>O, filtering with suction, washing with H<sub>2</sub>O and drying *in vacuo* at 80-90°; they are somewhat hygroscopic and slowly absorb O from the air. Lead, (C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>)<sub>2</sub>Pb, becomes light yellow after several weeks in the air; manganese, light flesh-colored when dry; cobalt, pale lavender, becomes dirty gray and gains in wt. in the air after several days; nickel, light green; chromium, dirty green; iron, light brown (the last 2 are apparently mixts. of A, the true salts and a little Na salt of A; found, 1.97-2.03 and 2.41-2.59% Cr and Fe, resp.; the buff-colored product obtained with FeCl<sub>3</sub> in 95% alc. instead of H<sub>2</sub>O contained 7.23-7.25% Fe and was completely sol. with deep red color in cold C<sub>6</sub>H<sub>6</sub> and raw linseed oil, while CrCl<sub>3</sub> in 95% alc. gave a bluish green salt with 14.93-15.16% Cr and practically insol. in C<sub>6</sub>H<sub>6</sub>). Excepting the last, all the above salts are sol. in C<sub>6</sub>H<sub>6</sub>, indicating the absence of any appreciable amt. of metallic hydroxides. C. A. R.

Color and chemical constitution. XII. Calculation of color from the tautomeric theory. JAMES MOIR. *Trans. Roy. Soc. S. Africa* 9, 205-16(1921); cf. *C. A.* 15, 4004.—The additive color relationships previously deduced are attributed to the motion of an electron, traversing with the velocity of light and in a sinuous orbit the series of alternate single and double linkings, of which the connection with depth of color has been previously indicated by Hewitt and Mitchell (*C. A.* 2, 130) and by Watson and Meek (*C. A.* 10, 454). The application of this conception to the case of aq. Michler's hydrol is represented by the diagram.



Additive values (indicated in brackets) are assigned to the tautomeric systems :C.CH:-C:(103 $\mu$ ), :C.CH:O(94 $\mu$ ), :C.CH:NH(98 $\mu$ ), :C.CH.NMe<sub>2</sub>(126 $\mu$ ) and to the modifications caused by substitution. These values are successfully applied to the cases of dihydroxybenzohydrol, benzaurine, diaminobenzohydrol, Doebner's violet, Michler's hydrol, malachite green, NaOPh, PhNH<sub>2</sub>, *o*- and *p*-NaOC<sub>6</sub>H<sub>4</sub>CHO, the phthaleins, the C<sub>10</sub>H<sub>8</sub> analogs of all these compds., indigotin, hydroxyazobenzene (as quinone phenylhydrazine) and its Na salt, and aminoazobenzene, and also to aurine, pararosaniline, and crystal violet, which have hitherto occupied an exceptional position. The cases of auramine, fuchsoneimonium chloride, and its di-Me deriv., and the higher azo dyes, however, still await an adequate explanation. J. C. S.

The molecular rearrangement of symmetrical bistriphenylmethylhydrazine. JULIUS STIEGLITZ AND RALPH L. BROWN. *J. Am. Chem. Soc.* 44, 1270-92(1922).—Org. N<sub>2</sub>H<sub>4</sub> derivs. resemble those of NH<sub>2</sub>OH in all fundamental characteristics except that, with the single exception of (Ph<sub>3</sub>CNH)<sub>2</sub> (A), they do not undergo mol. rearrangements of the type of the Beckmann oxime and the Lossen hydroxamic acid rearrangement. When A is heated to 250-300° with ZnCl<sub>2</sub> and the product is hydrolyzed PhNH<sub>2</sub> is obtained (cf. *C. A.* 11, 335); the only other product identified was Ph<sub>3</sub>CH, a product of a parallel thermal decompn. of the A. The present paper is a report of the continuation of the study of this reaction. By analogy to other rearrangements of this type



2 possible courses of the reaction suggest themselves at once: (I) According to S.'s theory, the primary reaction, offering the least resistance, might be a decompn. of the A into  $\text{Ph}_2\text{CNH}_2$  and the univalent N deriv.  $\text{Ph}_2\text{C:N}$  which would undergo the rearrangement proper into  $\text{Ph}_2\text{C:NPh}$ ; the last compd., on hydrolysis, should give  $\text{PhNH}_2$  and  $\text{Ph}_2\text{CO}$ . Or (II), there might occur a rearrangement similar to that of  $\text{Ph}_2\text{C.O.O.CPh}_2$

(Wieland, *C. A.* 5, 3821);  $\text{A} \longrightarrow 2\text{Ph}_2\text{C:NH} \longrightarrow 2\text{Ph}_2\text{CNHPh} \longrightarrow [\text{Ph}_2\text{C(NHPh)}]_2$ ; hydrolysis of the product should then give  $\text{PhNH}_2$  and  $[\text{Ph}_2\text{C(OH)}]_2$ . As a matter of fact, besides  $\text{PhNH}_2$ ,  $\text{Ph}_2\text{CO}$  has now been isolated from the product of hydrolysis. The 3rd product,  $\text{Ph}_2\text{CNH}_2$ , which should be formed according to reaction I could not be detected, but it has been found that  $\text{ZnCl}_2$  decomp.  $\text{Ph}_2\text{CNH}_2$  at the temp. of the above reaction chiefly into  $\text{NH}_3$ ,  $(\text{C}_6\text{H}_5)_2\text{CHPh}$  and  $\text{Ph}_3\text{CH}$ , and these 3 substances have been found among the products of the rearrangement of A. Thus far, all the evidence favored the view that the rearrangement of A proceeds according to reaction I. Exhaustive investigation of the reaction products, however, brought further facts to light. The reaction  $\text{A} \longrightarrow 2\text{Ph}_2\text{CH} + \text{N}_2$  previously observed was now shown conclusively to be a thermal decompn. The electronic interpretation given in the earlier paper shows that this decompn. is the result of an intramol. oxidation-reduction in which electrons migrate from the N to the methyl C atom, while the mol. rearrangement, considered from the electronic point of view, is also an intramol. oxidation-reduction, in which, however, the electrons migrate from the methyl C atom to the N. Among the reaction products phenol was obtained in appreciable quantities. Expts. with  $\text{Ph}_2\text{C:NPh}$  and  $\text{ZnCl}_2$  showed that this is not the source of the PhOH. Moreover, when A is heated with  $\text{ZnCl}_2$  in the absence of air (e. g., in  $\text{CO}_2$ ) no PhOH is produced but the formation of  $\text{Ph}_2$  is strongly suggested by the odor, and under these conditions the A undergoes no rearrangement into a  $\text{PhNH}_2$  deriv. Assuming, simply as a working hypothesis, that the reaction proceeds according to reaction I and that the formation of PhOH is due to the oxidation of Ph groups escaping rearrangement, then for every mol. of  $\text{Ph}_2\text{CNH}_2$  formed there should be produced either a mol. of  $\text{Ph}_2\text{C:NPh}$  or a mol. of PhOH. The amt. of  $\text{Ph}_2\text{CNH}_2$  formed was found by quant. detg.  $\text{NH}_3$ , the product of its decompn., that of  $\text{Ph}_2\text{C:NPh}$  by detg. the  $\text{PhNH}_2$  resulting from its hydrolysis and that of PhOH volumetrically. The results agree well with the above hypothesis.

C. A. R.

The electron theory of valence as applied to organic compounds. JULIUS STRICKLITZ. *J. Am. Chem. Soc.* 44, 1293-313(1922).—The evidence in favor of the theory of polar vs. non-polar valences in org. compds. as applied to various groups of derivs. is considered. In the mol. rearrangement of  $(\text{Ph}_2\text{CNH})_2$  (cf. preceding abstr.) the theory of polar valence gives an evident cause for the rearrangement, revealing a "fault" in the mol., and also makes evident the intramol. oxidation and reduction of certain atoms demanded by the exptl. results. These are fundamental advantages of the theory of polar as against that of non-polar valences in C compds. Exactly the same invaluable advantages of the theory of polar valences are found in the analogous mol. rearrangements of chloro- and bromoamides,  $\text{NH}_2\text{OH}$  derivs., peroxides, etc. In the wholly one-sided absorption reactions of  $\text{CO}_2$  and of innumerable org. compds. contg. unsatd. groups (C:O, C:S, C:N), polar valences are recognized as the uniformly directing forces. Similar directing forces are observed in absorptions by olefins, in which polar valences exist in the C to C unions. Exceptions to one-sided absorption as in the case of  $\text{BrCl}$ , are discussed and accounted for. The Crum Brown-Gibson rule of substitution in the  $\text{C}_6\text{H}_5$  series is developed on the basis of a polar electronic structure for  $\text{C}_6\text{H}_5$  which does not require the assumption of negative H (Fry) and is based on the application to  $\text{C}_6\text{H}_5$  of results firmly established in the aliphatic series. The different behavior of a negative halogen (e. g., in  $\text{RX}^-$ ) and of positive halogen (as in

RNHX<sup>+</sup>) is further important evidence in favor of polar valences even in the absence of ionization. Advantages of the polar structure for NH<sub>4</sub>OH and its derivs. are summarized. Evidence of the complete polar structure of acids, such as H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and of the CO<sub>2</sub>H group of org. acids is found in Faraday's observation of the deposition of S at the negative electrode in the electrolysis of concd. H<sub>2</sub>SO<sub>4</sub>, in Bird and Diggs' use of white P as the equiv. of a metal for producing an elec. current, and in the production of currents by using org. compds. as the source for the escape of electrons in oxidation-reduction cells. In the oxidation and reduction of org. compds. at room temp. the same general laws hold as for inorg. compds., *i. e.*, the *exposed* valences in org. compds. on double and triple bonds, in bi- and tervalent C, etc., are the common seat of oxidation and reduction reactions, especially at room temp. While polarity in org. compds. is an invaluable guide in following org. reactions, the polarity need not be of the extreme character shown by the common salts but may very well be of the character proposed by Bohr, Lewis and Kossel, where the transfer of electrons from atom to atom is not as complete as in the case of common electrolytes. Polarity exists, nevertheless, and the application of the theory of polar valence represents a decided advance in the interpretation of reactions of org. compds.

C. A. R.

**Ethylenic stereoisomerism.** CH. DUFRAISSE. *Ann. chim.* 17, 133–221 (1922); cf. *C. A.* 15, 670.—Attention is called to the very small vol. of research on geometric isomers as compared with optical isomers; of the former scarcely 200 have been prepd. Theoretical difficulties in the interpretation of known facts and practical difficulties in the discovery of new facts seem to be the principal causes for the slowness of progress of ethylenic stereochemistry. *I. Ethylenic isomers of dibromo- and di-iodobenzalacetophenone.*—PhCOCl in Et<sub>2</sub>O reacts rapidly with the evolution of heat when added to PhC: CNa in Et<sub>2</sub>O (prepd. by adding Na to PhC: CH in Et<sub>2</sub>O at –15°), forming PhCOC: CPh (C), m. 49°, in 64% yield. AcOH is added to decomp. the NaCl addition product and C is purified by fractional distn. A mixt. of two stereoisomeric dibromoacetophenones, (A) and (B), is obtained by adding Br<sub>2</sub> in CHCl<sub>3</sub> slowly to C in CHCl<sub>3</sub>. This yields large crystals, easily sorted by hand, from petr. ether by slow crystn. These are further purified by recrystn. from EtOH. A, prisms, m. 113–4°, insol. in H<sub>2</sub>O, slightly sol. in cold EtOH and in petr. ether, sol. in hot EtOH and various org. solvents. B, pale yellow pyramids usually joined base to base, m. 79–80°. A changes partially to B at 250° and the reverse occurs in the presence of I<sub>2</sub>. The transmutation is reversible in the sunlight. Nef (*Ann.* 308, 284) described a di-iodobenzalacetophenone (D) resembling A, easily obtained by adding I<sub>2</sub> in Et<sub>2</sub>O to Cin Et<sub>2</sub>O, prisms m. 140° (decompn. 155–6° (Maquenne block)). After careful study D. concludes that both isomers are formed primarily and that the quantity of the second (E) remaining is greatest in concd. soln. 4.8 g. I<sub>2</sub>, 4 g. C and 25 drops CS<sub>2</sub> are heated at 50° with const. shaking until the mixt. liquefies and the CS<sub>2</sub> evaps., then quickly transferred to a boiling satd. NaCl bath. The reaction is complete in a moment. The usual methods of sepg. isomers are useless but by adding a crystal of the more sol. E to a slightly supersatd. soln. of the mixt. E alone seps. (yield 20%) and can be readily purified by repeating this process. On the other hand if D is used to seed the soln. D and E sep. together. E is dimorphous, E<sub>α</sub> closely resembling B so that B can be used to seed out E. E<sub>α</sub>, citron-yellow hexagonal pyramids joined base to base, m. 70–1°, easily sol. in org. solvents. E<sub>β</sub>, hexagonal plates frequently grouped like pages of a book, m. 84–5°, less sol. than E<sub>α</sub>. The latter is obtained by rapidly cooling hot satd. solns. or by rapid evapn. E<sub>β</sub> is obtained by heating E<sub>α</sub> at 70–83°, by slow evapn. or by allowing a satd. soln. to stand in contact with solid E<sub>α</sub> for several hrs. E is partially transformed with decompn. to D at 140°. *II. Crystallography of B and E<sub>α</sub>.*—The crystal measurements of B are compared with those of E<sub>α</sub>. B crystals in four distinct variations of the hexagonal pyramids. *III. Prepara-*

tion, properties and constitution of two monobromobenzalacetophenones.—Monobromobenzalacetophenone (F), obtained by passing HBr into C in cold AcOH, pale yellow hexagonal plates m. 41–2°, easily sol. in org. solvents, closely resembles the bromobenzalacetophenone (G) obtained by Wislicenus (*Ann.* 308, 226) but is a distinct compd. since a mixt. of the two is an oil. G heated with alc. NaOH gives 2 mols. BzONa, 1 mol. PhC:CH and 1 mol. of one of the styrolene bromides (H). Previous work on the structure of the styrolene bromides being unsatisfactory D. establishes their constitution by a new, stereochem. method which promises to be useful. It consists essentially in the addition of two atoms of Br to the double bond. Stereoisomers give the same compd. while structural isomers give different compds. This method largely precludes any errors due to migration. A method is given describing the use of a new app. for crystn. and filtration at low temps.  $\omega$ -Bromostyrolene (I), obtained by decompn. of PhCHBrCHBrCO<sub>2</sub>H with hot aq. Na<sub>2</sub>CO<sub>3</sub>, pale yellow oil, m. 6–7°.  $\alpha$ -Bromostyrolene (J), obtained by passing HBr (80% of theory) into PhC:CH at 0°, slightly yellow lachrymatory oil, m. –44° to –43°. It is easily oxidized in air, thus being difficult to prep. and keep. H differs from these two and is shown to be a pure compd. by its const. m. p. on recrystn. These isomers all contain Br in the chain. The phenyltribromoethanes obtained from H and I are identical, m. 36.5–7.5° (Fittig, *Ann.* 195, 142). 1-Phenyl-1,1,2-tribromoethane, obtained by adding Br<sub>2</sub> to J, cannot be distd. in *vacuo* but must be purified by crystn. from MeOH at –80°. It is an oil of very faint odor, m. 5–6°,  $d_{16}^{20}$  2.0984,  $n_D^{21.7}$  1.6421, mol. refractivity 59.3. Since the theory accounts for two isomeric  $\omega$ -bromostyrolenes and one  $\alpha$ -bromostyrolene, H is PhCH:CHBr. Then G is PhCOCBr:CHPh which is contrary to Wislicenus. The action of NaOH on G is probably: PhCOCBr:CHPh  $\rightarrow$  PhCOCH(OH):CHPh  $\rightarrow$  PhCOCH<sub>2</sub>CHPh.

COPH (cf. *Ann.* 308, 226). F treated with Br gives the compound PhCOCHBrCBr<sub>2</sub>Ph, m. 98–9°, while G gives the compound PhCOCBr<sub>2</sub>CHBrPh, m. 103–4°. These are distinct chemically, proving F to be PhCOCH:CBrPh. IV. The stereoisomers of C and its two monobromo derivatives.—The prepn. of the geometric isomers of C, F and G and also the isomerization of C, F, and G was attempted without the successful sepn. of the second isomers. V. The geometric isomerism of the  $\omega$ -bromostyrolenes.—The stereoisomerism of H and I is discussed fully; they are in equil. at ordinary temps. and the equil. is rapidly reached in the light. VI. Stereochemical considerations.—The benzalacetophenone stereoisomers are compared as to color, crystallography and transmutation. The addition and eliminations reactions as well as the relations of m. p. to color and stability also are reviewed. There is still some doubt as to which compds. are *cis* and which *trans*.  
T. E. DUNLAP

Atomic vibrations in the molecules of benzenoid substances. R. ROBINSON. *Nature* 109, 476(1922).—The view is advanced that the structure suggested by Bragg (*Proc. Phys. Soc.* 34, 33(1921)) for the mol. of crystd. C<sub>6</sub>H<sub>6</sub> is not a stable one but rather represents a phase of an oscillation of the relatively unrestricted mols. in which the pairs of C atoms in the positions designated *k*, *a*, and *f*, *d* appear alternately above and below the plane contg. the 6 remaining atoms.  
W. H. ROSS

Configurations of molecules of benzenoid substances. J. KENNER. *Nature* 109, 581(1922).—Exptl. evidence has been obtained, to be published in detail later, that in the sep. mols. of benzenoid substances the 2 C<sub>6</sub>H<sub>6</sub> nuclei are not coplanar. If this be so then it follows that the direction of the valency of each of the C atoms through which these nuclei are united is not, as represented in the usual formulas for C<sub>6</sub>H<sub>6</sub>, exerted in the plane of the C<sub>6</sub>H<sub>6</sub> ring, and further that this condition is a stable one rather than a phase of an oscillation of the type referred to by Robinson (preceding abstr.).  
W. H. ROSS

**Naphthalene derivatives.** R. SCHOLL, C. SKEER, R. WEITZENBÖCK AND A. ERTL. *Monatsh.* **42**, 405-9 (1922).—5-Iodo-1-nitronaphthalene (A), prepd. by diazotizing 1,5-O<sub>2</sub>NC<sub>10</sub>H<sub>6</sub>NH<sub>2</sub> and pouring the filtered soln. into KI soln., subliming in a CO<sub>2</sub> stream and crystg. from AcOH, fine, straw-yellow needles, m. 164°, reduced in AcOH-HCl by granulated Zn to 5-iodo-1-naphthylamine, leaflets, m. 75°; sulfate, fine needles, turning red in the air, m. 205-15° (decompn.); hydrochloride, fine needles, turning blue in the light. 5-Iodo-1-naphthol, by boiling the diazo compd. from the amine with 20 % H<sub>2</sub>SO<sub>4</sub>, fine needles from hot H<sub>2</sub>O, m. 131-2° and volatile in steam. The yield is low, owing to resin formation, and a compound, perhaps diiodoazonnaphthol, dark red needles from C<sub>6</sub>H<sub>6</sub>, m. 228-245°. 5-Iodo-1-naphthol methyl ether, needles from dil. MeOH, m. 78-9°. A, heated with an equal amt. of Cu powder at 220-30° for 5 hrs., gave 5,5'-dimitro-1,1'-binaphthyl, light brown, glistening leaflets, m. 228-8.5°. 1,8-Dibromo-2,7-dihydroxynaphthalene, fine needles, m. 156-8° (decompn.). Dibenzozate, needles m. 209°. 5-Nitro-1-naphthonitrile (*Ber.* **16**, 2246) was prepd. by diazotizing 5,1-O<sub>2</sub>N-C<sub>10</sub>H<sub>6</sub>NH<sub>2</sub> and treating with KCN-CuCN soln., in a yield of 32 %. 5-Nitro-1-naphthylazide (*J. Chem. Soc.* **91**, 1948) was more conveniently prepd. by diazotizing 5,1-O<sub>2</sub>N-C<sub>10</sub>H<sub>6</sub>NH<sub>2</sub> and treating with aq. NH<sub>2</sub>OH (yield 55 %). The sodium salts of normal and iso-5-nitro-1-diazonnaphthalene hydrate are described. C. J. WEST

**Reduction of naphtholcarboxylic acids to aldehydes.** HUGO WEIL AND WALTER HERBERT. *Ber.* **55B**, 224-30 (1922); cf. C. A. **16**, 1947.—2,3-C<sub>10</sub>H<sub>6</sub>(OH)CO<sub>2</sub>H with 5.5 g. soda in a little H<sub>2</sub>O and 80 cc. of 40% NaHSO<sub>3</sub> almost neutralized to litmus with NaOH, dild. to 1 l., treated with 15 g. H<sub>3</sub>BO<sub>3</sub> and 100 g. NaCl, cooled to -5° and reduced by gradual addition of Na-Hg (the soln. being kept faintly acid with HCl), consume about 100 g. of the Na-Hg in 3 days and yield tetrahydronaphthalene-2-aldehyde whose hydrazone m. 106.5° after recrystn. from alc. containing a little AcOH (given as 96.5° in the earlier paper). The same product is obtained from 2,3-C<sub>10</sub>H<sub>6</sub>(OAc)CO<sub>2</sub>H. 1,2,3-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)(OH)CO<sub>2</sub>H is obtained in 60% yield by treating 38 g. 2,3-C<sub>10</sub>H<sub>6</sub>(OH)(OH)CO<sub>2</sub>H in 40 g. calcined soda and 400 cc. H<sub>2</sub>O with 35 g. sulfanilic acid in 11 g. soda and 100 cc. H<sub>2</sub>O, diazotized by treating with 14 g. NaNO<sub>2</sub> and pouring into 30 cc. concd. H<sub>2</sub>SO<sub>4</sub> and 200 cc. H<sub>2</sub>O, and reducing the pptd. dye in dil. AcOH with Zn dust at 50°; reduction of the NH<sub>2</sub> acid with Na-Hg as above gives NH<sub>3</sub> and the above aldehyde. 1-Bromo- and 1-chloro-2,3-naphtholcarboxylic acids give the same aldehyde. 1,2-C<sub>10</sub>H<sub>6</sub>(OH)CO<sub>2</sub>H and the acetate, reduced like the 2,3-compd. at 25°, 40° and 55° never gave anything but 1,2-C<sub>10</sub>H<sub>6</sub>(OH)CHO. 4,1,2-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)(OH)CO<sub>2</sub>H, decomps. 230°, is so feebly acidic that it is liberated and quant. pptd. from its soda salt by H<sub>2</sub>BO<sub>3</sub> and cannot therefore, be reduced by the above method. 1,2,4-C<sub>10</sub>H<sub>6</sub>(OH)(CO<sub>2</sub>H)SO<sub>3</sub>H loses its SO<sub>3</sub>H group and gives 1,2-C<sub>10</sub>H<sub>6</sub>(OH)CHO. 4,1,2-C<sub>10</sub>H<sub>6</sub>Br(OH)CO<sub>2</sub>H yields 30% of a substance consisting chiefly of the bromo aldehyde (A), which in spite of repeated crystn. is somewhat low in Br (found, C 54.6, H 3.1, Br 30.5%). 4-Chloro-1,2-naphtholcarboxylic acid, m. 228°, obtained in 85% yield from C<sub>10</sub>H<sub>6</sub>(OH)CO<sub>2</sub>H in AcOH with Cl, gives 50% of the aldehyde (B). Condensation products of A with: ammonia, C<sub>22</sub>H<sub>18</sub>O<sub>2</sub>N<sub>2</sub>Br, yellow crystals from Et<sub>2</sub>O, m. 126°, rapidly blackens (decompn.); phenylhydrazine, yellow leaflets from alc., m. 159°; aniline, orange-yellow needles from alc., m. 161°; o- and p-toluidine, yellow-red needles, m. 188° and 171°, resp.; benzidine, red leaflets from alc., m. 218°; α-naphthylamine, red needles from alc., m. 196°; o-, m- and p-phenylenediamine, yellow to red, m. 225°, 201° and 198°. Condensation products of B with: ammonia, yellow, sol. without decompn. in alc. but decomps. into NH<sub>3</sub> and B on moderate warming in H<sub>2</sub>O, acids or alkalis; hydroxylamine, needles, m. 184°; hydrazine, yellow needles, m. 179°; phenylhydrazine, yellow leaflets, m. 153°; aniline, yellow needles, m. 157°; o- and p-toluidine, orange-yellow, m. 183° and 164°; α-naphthylamine, red-yellow leaflets, m. 188°; benzidine, red, m. 214°; o-, m- and p-phenylenediamine,

ine, yellow to red leaflets, m. 221°, 250° and 240°. Sodium salt of B, from 2 g. B with 1 g. NaOH in the least possible amt. of H<sub>2</sub>O, yellow leaflets. C. A. R.

Theory of the *cis-trans*-isomerism of decahydronaphthalene. ERNST MOHR. Ber. 55B, 230-1 (1922).—Willstätter and Waldschmidt-Leitz (C. A. 15, 3830) believe that only *cis*- but not *trans*-decahydronaphthalene is capable of existence. M. has recently described an entirely strain-free model for each form (C. A. 13, 2861). In their properties, especially as regards stability and heat of combustion, the 2 isomers would probably show very little differences, if any. Neither can be optically active, as can be seen from Figs. 5 and 6 of the paper referred to. The same considerations hold for the derivs. of decahydronaphthalene; 8 perfectly strain-free models of decahydro- $\beta$ -naphthol and 32 strain-free, structurally identical models of perhydronaphthylmethane-*o*-benzoic acid can be constructed. The fact that up to the present no observations have been made which necessitate the assumption of *cis-trans*-isomerism in this series of compds. should not restrain investigators from searching for a 2nd decahydronaphthalene and its derivs. C. A. R.

Anthraquinone and its derivatives as reductive catalysts. CHARLES SUNDER AND MARCEL BADER. Bull. soc. ind. Mulhouse 87, 187-9 (1921).—The facility with which anthraquinone is reduced to anthraquinol and the ready oxidizability of the latter render it an excellent H carrier for the hydrogenation of difficultly reducible substances such as  $\alpha$ -naphthaleneazo- $\beta$ -naphthol. This property is not exhibited to the same extent by a considerable number of derivs. of anthraquinone which have been examd.; on the other hand, 2-hydroxyanthraquinone is somewhat more active than the parent substance. J. C. S.

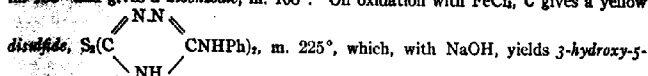
Chief constituent of Japanese lac. VIII. Position of the double bonds in the side chain of urushiol and proof that urushiol is a mixture. RIKO MAJIMA. Ber. 55B, 172-91 (1922); cf. C. A. 15, 883.—Although the structure of hydrourushiol (A), the reduction product of urushiol (B), has been established, the position of the double bond in the side chain of B itself has not yet been detd. Oxidation of the di-Me ether of B with O<sub>2</sub> has given AcH, heptanal, CO<sub>2</sub>, heptanic acid, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>7</sub>CHO(?), (CO<sub>2</sub>H)<sub>2</sub>, and azelaic acid (C. A. 4, 203), but the yield of aliphatic products was small. It has now been found that when diacetylurushiol is ozonized in CHCl<sub>3</sub> and steam distd. without isolating and purifying the ozonide diacetylhydrourushiol is present among the products of the decompn. of the crude ozonide, a fact which can be explained only on the assumption that B is not homogeneous but contains some A; the other products are the same as those which had been obtained from the di-Me ether. Monoacetylurushiol mono-Me ether (purified with especial care) with O<sub>2</sub> gives heptanal, heptanic acid, AcO(MeO)C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>7</sub>CHO(?), monoacetylhydrourushiol mono-Me ether and  $\omega$ -[3-methoxy-1-hydroxyphenyl]caprylic acid (C); no AcH was found. With KMnO<sub>4</sub> the di-Me ether of B gives heptanal, HCO<sub>2</sub>H and lower fatty acids, (CO<sub>2</sub>H)<sub>2</sub>, adipic and suberic acids, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>7</sub>CO<sub>2</sub>H(?), the di-Me ether of A and 2,3-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, the latter product establishing beyond doubt the structure which had been assigned to A. In view of the formation of HCO<sub>2</sub>H, the oxidation of the di-Me ether of B with O<sub>2</sub> was repeated and found to give HCO<sub>2</sub>H also, as well as AcH. When a large amt. of the di-Me ether was carefully fractionated in a high vacuum and the higher fractions were ozonized, there were obtained, instead of AcH, a little HCHO and a very small amt. of CO<sub>2</sub>, together with HCO<sub>2</sub>H. The di-Me ether easily adds about 4 atoms Br (a small amt. apparently substitutes in the nucleus), and since with stearic acid the last 2 atoms of Br add very much more slowly than the first 2, it is concluded that there is no C:C bond in B. In the repeated fractionation of a large amt. of the Me ether of B was obtained a small amt. of a hydrocarbon, C<sub>14</sub>H<sub>22</sub> or C<sub>14</sub>H<sub>24</sub>, of characteristic odor, called *urusene* (D). M. concludes that B, the chief constituent of Japanese lac,

contains up to 10% A and probably the compds.  $(\text{HO})_2\text{C}_6\text{H}_7(\text{CH}_2)_7\text{CH} : \text{CH}(\text{CH}_3)_2\text{Me}$  (E) and  $(\text{HO})_2\text{C}_6\text{H}_7(\text{CH}_2)_7\text{CH} : \text{CH}(\text{CH}_3)_4\text{CH} : \text{CH}_2$  (F); although E and F are present along with C in B the compn. of the bromides and ozonides obtained from the di-Me ether and the amt. of O absorbed in the reduction would seem to indicate that it has 2 double bonds; therefore, in addition to A, E and F, it must contain a still more unsatd. compd. (G) with another double bond between the two in F, or only G is present along with A and E; B is therefore a mixt. of compds. differing from each other only in the no. and positions of double bonds in a long normal C chain, thus showing a marked similarity to the drying oils, and making a quant. sepn. of its components by our present chem. methods a practically hopeless task, but as they all yield the same A on reduction it seems well to retain the name "urushiol" for the original mixt. and to assign to it the av. mol. formula  $(\text{HO})_2\text{C}_6\text{H}_7\text{C}_{15}\text{H}_{27}$ . Diacetylurushiol can be obtained pure (26 g. from 71 g. crude product) by distg. under 0.3 mm., where it b.  $212-20^\circ$ . Among the products of its ozonization is obtained an oil, b<sub>1</sub>  $205-7^\circ$ , mol. wt. in boiling  $\text{Et}_2\text{O}$  342-66, AcO found (Wenzel method) 23.8%, which is apparently  $\omega$ -[2,3-diacetoxyphenyl]-caprylaldehyde; it shows strong aldehyde properties, blackens with alkali in alc. but gives no color with  $\text{FeCl}_3$ , gives on oxidation in  $\text{Me}_2\text{CO}$  with  $\text{KMnO}_4$  to disappearance of the aldehyde reactions an acid showing the various color reactions of B and, on further oxidation, azelaic acid. The substance obtained in the ozonization of monoacetylurushiol Me ether which is supposed to be  $\omega$ -[2-acetoxy-3-methoxyphenyl]caprylaldehyde is a brownish yellow, somewhat fluorescent oil, b<sub>0.5</sub>  $190-210^\circ$ , 4.4 g. of which with 1.6 g.  $\text{KMnO}_4$  and 1 cc. AcOH in  $\text{Me}_2\text{CO}$  gives 0.7 g. of C, needles from petr. ether, m.  $49-50^\circ$ , gives a greenish blue color with  $\text{FeCl}_3$  in alc.  $\omega$ -[2,3-Dimethoxyphenyl]caprylic acid, obtained in the  $\text{KMnO}_4$  oxidation of the di-Me ether of B, was isolated through the methyl ester, b<sub>0.5-0.5</sub>  $173-93^\circ$ . D b<sub>15</sub>  $130-7^\circ$ , mol. wt. in freezing  $\text{C}_6\text{H}_6$  202-7, absorbs Br. IX. Chemical investigation of different natural lacs which are closely related to Japanese lac. *Ibid* 191-214.—A crude black Burmese lac (which is of better quality than the brown or red forms), known as "thitsi" and obtained from *Melanorrhea usitata* Wall, was dissolved in alc., filtered, evapd. and extd. with much petr. ether, the black-brown oil which dissolves being called *thitsiol* (A). At first sight there would seem to be no great difference in chem. behavior between A and urushiol (B) but the *hydrothitsiol* (C) obtained by its catalytic hydrogenation differs in m. p. and compn. from hydrourushiol (D); it has the compn.  $(\text{HO})_2\text{C}_6\text{H}_7\text{C}_{17}\text{H}_{33}$  and belongs to the isohydrourushiol (E) series and was proved by synthesis to be 3,4-dihydroxy-1-heptadecylbenzene, indicating that A contains a homolog, with an unsatd. side chain, of E, but this can amount at most to only  $1/3$  of the A, for the yield of C and its di-Me ether is very small. Similarly, A gives but a small amt. of ozonide; the nature of the non-ozonizable part has not yet been cleared up. Laccol (F), similarly prepd. from Indo-Chinese lac (which is probably obtained from *Rhus succedanea*), resembles B in appearance and chem. reactions but differs somewhat in compn. *Hydrolaccol* (G) with  $\text{KMnO}_4$  gives stearic acid and is therefore probably 2,3-dihydroxy-1-heptadecylbenzene. The di-Me ether of F on ozonization yields, besides aromatic decompn. products,  $\text{HCO}_2\text{H}$ , enanthal and nonane- $\omega,\omega$ -dicarboxylic acid, confirming the conclusion that F has 2 more  $\text{CH}_2$  groups in its side chain than E. The portion of the ether not attacked by  $\text{O}_3$  contains the di-Me ether of G. Formosa lac, from *Semeocarpus vernicifera*, and tsuta-urushi lac, from *R. ambigua* Lav. or *R. orientalis*, also contain F as the chief constituent. The chief constituent of 2 samples of pure Chinese lac, probably obtained from *Rhus vernicifera* or a very closely allied species, was found to be identical with B. F is a brown thick liquid,  $\text{C}_{22}\text{H}_{30}\text{O}_2$ ; dimethyl ether (37 g. from 45 g. F with  $\text{NaOEt}$  and  $\text{MeI}$  in a H atm. on the  $\text{H}_2\text{O}$  bath), b<sub>0.25</sub>  $206-8^\circ$ ,  $d_4^{25}$  0.92954. G (7.2 g. from 10 g. F in  $\text{Et}_2\text{O}$  with H and Pt black), crystals from petr. ether, m.  $63-4^\circ$ ; 6 g. with  $\text{KMnO}_4$  in  $\text{Me}_2\text{CO}-\text{H}_2\text{O}$  yields 1.4 g.

stearic acid; *dimethyl ether*, from the ether of **F** with H and Pt black, long, flat prisms from alc., m. 43-4°, gives with concd.  $\text{HNO}_3$  in AcOH on short warming a *5-nitro derivative*, crystals from alc., m. 75-6°, which with concd.  $\text{HNO}_3$  (d. 1.48) yields the *5,6-dinitro compound*, crystals from alc., m. 86-7°. The di-Me ether of **F** (33 g.) treated in  $\text{CHCl}_3$  at -10° with 7%  $\text{O}_3$  yields 28 g. of a *mono-ozonide* which on decompn. with  $\text{H}_2\text{O}$  under a reflux gives heptanal, AcH,  $\text{HCO}_2\text{H}$  (7 g. of the Pb salt from 27 g. ozonide), 1.3 g.  $(\text{CO}_2\text{H})_2$ , a substance with aldehyde reactions b.p. 25-0.27 170-4° (apparently impure  $(\text{MeO})_2\text{C}_6\text{H}_3(\text{CH}_2)_7\text{CHO}$ ), nonane-4,9-dicarboxylic acid, crystals from  $\text{CHCl}_3$ , m. 109-11°, and a  $\text{H}_2\text{O}$ -insol. acid, m. 42°, whose Me ester b.p. 150-80°; the petr. ether soln. used in purifying the ozonide yielded 2.9 g. of the di-Me ether of **G**. **A**,  $\text{C}_{22}\text{H}_{40}\text{O}_3$ , gives on methylation 49% of its wt. of the *dimethyl ether*, b.p. 204-5°, d. 0.96390. **C** (5 g. from 25 g. **A**), crystals from petr. ether, m. 94-6°, gives in alc. with  $\text{FeCl}_3$  a green color, with KOH a blue, then a red color; *dimethyl ether* (5.5 g. from 48 g. of the ether of **A**), flat leaflets from alc., m. 56-7°, smoothly demethylated by heating 2 hrs. with HBr (d. 1.78), gives with  $\text{HNO}_3$  in AcOH a *6-nitro derivative*, faintly yellowish needles from alc., m. 75-6°, decompn. when heated with concd.  $\text{HNO}_3$ ; a product identical with the ether is obtained in 1.4 g. yield by reduction with amalgamated Zn of *hexadecyl pyrocatechyl ketone*, m. 100-3°, which in turn is obtained in 1.7 g. yield from 5 g. *gumargic acid* and 5 g. *pyrocatechol* heated with 10 g.  $\text{SnCl}_2$ . *Thitsiol dimethyl ether diazonide* (3.5 g. from 15 g. of the ether); 6 g. on decompn. yielded 0.1 g.  $(\text{CO}_2\text{H})_2$  as the only product which could be identified; the petr. ether- $\text{Et}_2\text{O}$  mother liquor from the ozonide from 30 g. **A** gave 26 g. of a thick oil from which were obtained 12 g. of a neutral product b.p. 200-40°. Some persons, on touching lac trees, the sap or freshly lacquered products, or even on merely stopping where the trees grow, develop a more or less severe inflammation of the skin, while other are entirely immune; old lacquered products are never toxic. Toyama (*Festschrift f. Prof. Dohi: Über die Lackkrankheit*, p. 3) has studied the cause of this toxicity and the chem. important part of his results is reported in the present paper. He confirmed Tschirch and Jadassohn's observation that the poison (*vernicoferol*) is not volatile, is present only in the petr. ether- and alc.-sol. portion and is pptd. by  $\text{Pb}(\text{OAc})_2$ . He found, moreover, that the toxicity of the crude lac does not decrease after standing 6-7 hrs. in  $\text{H}_2\text{O}$  or when treated with steam; the smoke produced by heating a lacquered sheet of Fe at 150-200° is not toxic. Hence it was concluded that the "*vernicoferol*" is identical with **B** and as a matter of fact purified **B** was found considerably more toxic than the crude lac. The toxicity decreases in the order **B**, **D**, di-Me ethers of **B** and **D**, the last being innocuous. **F** and **A** are about equally toxic but less so than **B**. The toxicity of pyrocatechol and its homologs increases with the mol. wt.\* of the side chain but is apparently independent of its position. C. A. R.

**Disulfides with neighboring single and multiple linkings. Syntheses of triazoles and thiodiazoles.** EMIL FROMM, ERICK KAYSER, KARL BRIEGLER, and ERICH FOHRNBACH. *Ann.* 426, 313-45 (1922); *J. Chem. Soc.* 122, 377.—The course followed by the reaction between bases and unsatd. disulfides of the type  $\text{X}:\text{CRS}_2\text{CR}:\text{Y}$  is, in general, that expressed by the equation:  $\text{X}:\text{CRS}_2\text{CR}:\text{Y} + \text{NH}_2\text{Ph} \rightarrow \text{X}:\text{CRSH} + \text{NHPhCR}:\text{Y} + \text{S}$ . **F** shows that the reactions between hydrazines and similar disulfides are of an analogous kind and may be utilized for the synthesis of triazoles and thiodiazoles. Thus phenyldithiobiuret may react with  $\text{N}_2\text{H}_4$  in 2 ways, eliminating 1 atom S and yielding either aminophenylguanidinothiurea (**A**), or aminoguanidinophenylthiurea (**B**). The former can pass into a triazole by elimination of either  $\text{H}_2\text{S}$  or  $\text{NH}_3$  but **B** can give only 3-amino-5-anilino-1,2,4-triazole. The principal product is actually 3-*thio-5-anilino-1,2,4-triazole* (**C**), needles from hot  $\text{H}_2\text{O}$ , m. 268°. This shows that the main product of the initial ring scission is **A**. The by-products obtained are 3-amino-5-anilino-1,2,4-triazole, m. 77° (benzoate, m. 142°), the salt, m. 70°, of the amino-

anilinotriazole with the thioanilinotriazole, and aminoguanidinophenylthiourea, m. 156° (benzylidene derivative, yellow needles, m. 223°). C gives a dibenzoate, yellow needles, m. 130°, and with  $\text{PhCH}_2\text{Cl}$  and alkali yields 5-anilino-3-benzylthio-1,2,4-triazole, m. 168°, and gives a dibenzoate, m. 108°. On oxidation with  $\text{FeCl}_3$ , C gives a yellow



anilino-1,2,4-triazole, m. 169° (dibenzoate, m. 166°), and C.  $\text{PhNH}_2$  effects a similar scission, the products being C and 3,5-dianilino-1,2,4-triazole, conveniently isolated as the dibenzoate, m. 88°. The action of  $\text{PhNHNH}_2$  on perthiocyanic acid has been shown by Fromm and Schneider to proceed in directions analogous to the reactions described above, the products being 3,5-dithio-1-phenyl-1,2,4-triazole (D) and 3-amino-5-thio-1-phenyl-1,2,4-triazole (E). Treatment of D with  $\text{MeI}$  and  $\text{NaOH}$  gives 3,5-dimethylthiol-1-phenyl-1,2,4-triazole, filamentous needles, m. 73.5°, which, with  $\text{KMnO}_4$ , yields 3,5-dimethylsulfone-1-phenyl-1,2,4-triazole (F), needles, m. 182°, together with a substance,  $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_4\text{S}_2$ , m. 104.5°, which may be either a monosulfone or a disulfide. F is unstable towards alkalis and loses 1 sulfone group, yielding 5-hydroxy-3-methylsulfone-1-phenyl-1,2,4-triazole (G), m. 206°, identical with the substance obtained on oxidizing Acree's 5-hydroxy-3-methylthiol-1-phenyl-1,2,4-triazole by means of  $\text{KMnO}_4$ . G, methylated by means of its  $\text{Ag}$  salt, gives the 5-methoxy derivative, fine needles from  $\text{EtOH}$ , m. 206°. The disulfone, in contrast to its behavior with alkalis, is very stable towards acids, and can be nitrated with the formation of 3,5-dimethylsulfone-1-nitrophenyl-1,2,4-triazole, m. 238°, which with alkalis is converted into a 5-hydroxy-3-methylsulfone-1-nitrophenyl-1,2,4-triazole, m. 234°, identical with the product obtained by directly nitrating G (see Ber. 37, 618(1904)). 3-Amino-5-methylthiol-1-phenyltriazole (H), needles, m. 148°, is prepd. from E and  $\text{MeI}$ ;  $\text{BzCl}$  and  $\text{C}_6\text{H}_5\text{N}$  give the 3-benzoyl derivative, m. 141.5°, also prepd. by methylating 5-thiol-3-benzoylamino-1-phenyl-1,2,4-triazole (C. A. 7, 794). A dibenzoate is formed when H is heated with  $\text{BzCl}$  until  $\text{HCl}$  is no longer evolved. The simplest members of the series to which the above substances belong are 3,5-dithiol-1,2,4-triazole (I) and 5-amino-3-thiol-1,2,4-triazole (J), which are both obtained as their  $\text{N}_2\text{H}_4$  salts when  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  is allowed to react with perthiocyanic acid. I and J may be sepd. by taking advantage of the fact that J is the weaker acid and is liberated in the free condition when its  $\text{N}_2\text{H}_4$  salt in  $\text{H}_2\text{O}$  is evapd. The  $\text{N}_2\text{H}_4$  salt of I is stable in these circumstances but may be decompd. by means of mineral acids or by  $\text{BzH}$ . J seps. from  $\text{H}_2\text{O}$  in small needles, m. 298° (decompn.). I, m. 196° (decompn.), has strongly reducing properties; it 1st reddens litmus paper and then bleaches it and quickly reduces I and  $\text{FeCl}_3$ . Lead salt, yellow; hydrazine salt, m. 268° (decompn.). With  $\text{BzCl}$  (Schotten-Baumann) J gives 5-imino-3-thion-2,4-dibenzoyl-1,2,4-triazole, yellow, m. 178°, while I gives 3,5-dithion-1,2,4-tribenzoyl-1,2,4-triazole, m. 171°, which on further treatment with  $\text{PhCH}_2\text{Cl}$  and  $\text{NaOH}$ , yields 3,5-dibenzylthiol-1,2,4-triazole (K), m. 112° (hydrochloride, m. 157°), the product of the direct benzylation of I. K, treated with  $\text{BzCl}$  (Schotten-Baumann) yields 4-benzoyl-3,5-dibenzylthiol-1,2,4-triazole, fine needles, m. 91°. Alkali eliminates all 3 Bz groups. All these reactions are in harmony with the constitution assigned to the original condensation products. An examn. of the substances,  $\text{C}_7\text{H}_5\text{N}_3\text{S}_2$  and  $\text{C}_7\text{H}_5\text{N}_3\text{S}$ , obtained by Freund and Ingart (Ber. 28, 946(1895)) from hydrazodicarboxidithioamide leads to the conclusion that they are not triazoles but thiodiazoles, isomeric, therefore, with the substances obtained from perthiocyanic acid and  $\text{N}_2\text{H}_4$ . 5-Amino-3-thion-4,1,2-thiodiazole (L) forms a lead salt, and on benzylation gives a 2,5-dibenzoyl derivative, m. 224°; on benzylation, fission of the ring occurs and benzyl benzylthio- $\psi$ -carbasinocarbothioylate,  $\text{C}_7\text{H}_5\text{SC}(\text{NH}_2) : \text{N}_2 : \text{C}(\text{OH})\text{SC}_6\text{H}_5$ , is formed, palm leaf-like crystals,



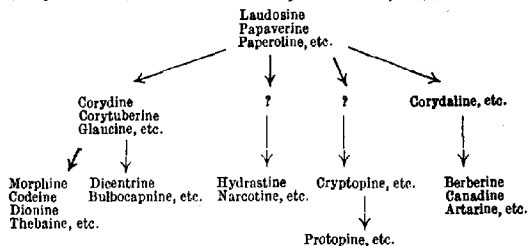
m. 193°, and on benzoylation gives an *anhydro-benzoate*, m. 123°, which may also be obtained by benzylating the above di-Bz compd. The m. p. of L is given as 223-35° and that for 3,5-diamino-4,1,2-thiodiazole as 210°.

C. J. Waser

**Isocyanines and carbocyanines: Their constitution and their activity as photographic sensitizers.** Wm. POPP. *Bull. soc. chim. Belg.* 30, 169(1921).—A lecture delivered under the auspices of the Solvay Chem. Institute on March 19, 1921.

J. C. S.

**Structural relation of isoquinoline and phenanthrene alkaloids.** I. W. D. HACKH. *Chem. News* 123, 178-9(1921).—The use of structure symbols (*C. A.* 12, 2318) reveals an interesting structural relationship among alkaloids contg. the isoquinoline nucleus. Alkaloids such as morphine, berberine, papaverine, glaucine, narcotine, corydaline, dicentrine, protopine, cryptopine, etc., appear to belong to different groups when the usual structural formulas are used, but when these structural formulas, or the corresponding structure symbols, are turned so that the isoquinoline nucleus occupies the same relative position in each, a structural relationship, which genetically connects all these alkaloids, may be traced, and the alkaloids may be classified, thus:



On this basis, Pschorr's formula for morphine is regarded as more probable than the formula of Freund and others.

J. C. S.

**Spontaneous decomposition of imido esters.** T. B. JOHNSON AND L. W. BASS. *J. Am. Chem. Soc.* 44, 1341-3(1922).—As is well known, imido esters dissociate, even at room temp., into nitriles and alcs. and it seems quite characteristic for the nitrile to undergo further change, finally almost completely polymerizing into the trimol. cyaphenin, while ordinarily nitriles, when free from impurities, are not unstable and where polymerization has been observed it has quite generally been induced by the action of a variety of polymerizing reagents or by heating at high temps. In imido ester decompns., there is present only one dissociation product (the alc.) to influence the polymerization; therefore in such cases the tendency to polymerize might be explained as due to the unsatd. condition of the nitrile at the moment of dissociation of the imido ester mol., the polymerization to  $(\text{PhCN})_3$  taking place before the free valences of the

unsatd. cyanide  $\text{PhC}:\text{N}$  (A) have readjusted themselves into the stable condition of the nitrile,  $\text{PhC}:\text{N}$ . Both changes (formation of nitrile and polymerized nitrile) are therefore to be expected in imido ester decompns. at room temp. The rearrangement of ordinary  $\text{PhCN}$  into  $(\text{PhCN})_3$  under the influence of polymerizing agents may also be interpreted as a case of disturbance of valence equil. in the nitrile by the catalyst, giving the unstable form A, which then immediately polymerizes. Wheeler and J. in 1900 sealed freshly prepd. and very carefully purified samples of  $\text{PhCN}$  and several imido esters in glass containers, the contents of which have now, after 22 yrs. storage, been examd. by J. and B. Neither the  $\text{PhCN}$  nor a sample of  $p\text{-MeC}_6\text{H}_4\text{CN}$  which had been kept several yrs. showed any change but with the imido esters there were found in

every case heavy deposits of the cyaphenin derivs. and the non-polymerized nitrile. In the case of  $\text{PhC}(\text{NH})\text{OMe}$  the change into  $(\text{PhCN})_3$  was practically quant.; the Et and iso-Bu esters yielded both  $\text{PhCN}$  and  $(\text{PhCN})_3$ ;  $p\text{-MeC}_6\text{H}_4\text{C}(\text{NH})\text{OMe}$  was almost completely converted into  $(\text{MeC}_6\text{H}_4\text{CN})_3$ . C. A. R.

A saponin from *Agave lechuguilla* (JOHNS, *et al.*) 11D. Chemical reactions caused by the silent discharge (MIYAMOTO) 2. The conjugation of partial valencies (ROBINSON) 2. Effecting chemical reactions (Brit. pat. 176,438) 13. Treating fruit kernels (U. S. pat. 1,416,128) 18.

BERNTSEN, A.: A Textbook of Organic Chemistry. New edition revized by J. J. Sudborough, London: Blackie & Son, Ltd. 908 pp. 12s 6d.

LÖWE, HANS: Die elektrochemische Oxydation des o-Toluolsulfamids zu Saccharin. Basel: E. Birkhäuser & Cie. 43 pp.

**Oxalates.** OLDBURY ELECTRO CHEMICAL CO. Brit. 174,126, Sept. 17, 1920. An alkali-metal formate is melted in a vessel at a temp. below  $295^\circ$ , at which conversion into oxalate begins, and is then transferred to a sep. conversion vessel, the temp. of which may be  $380\text{--}440^\circ$ , so that conversion is rapidly effected. The formate may be preheated to  $270^\circ$  in the first vessel. A caustic alkali or other substance promoting conversion may be added to the formate after melting. Cf. 160,747 (C. A. 15, 2286).

**Borneol.** A. HALLER. U. S. 1,415,340, May 9. Tetrachlorophthalic acid is heated in a reflux app. with crude pinene for 12 hrs. at  $106\text{--}108^\circ$  and then for shorter times at  $125^\circ$  and  $140^\circ$ . After cooling, unchanged terpenes are distd. off by heating up to  $140^\circ$ , leaving a residue (which when cooled has the brilliancy of glass and somewhat resembles colophony) consisting mainly of the di-bornyl ester of tetrachlorophthalic acid, which by sapon. with NaOH in alc. yields borneol. The alc. is distd.,  $\text{H}_2\text{O}$  is added and the pptd. borneol is filtered, washed with  $\text{H}_2\text{O}$  and centrifuged.

**Dehydrating pyridine.** W. J. HUFF. U. S. 1,416,205, May 16. An aq. fraction is distd. from the pyridine, this fraction is dehydrated by the action of a  $\text{H}_2\text{O}$ -absorbing salt and the dehydrated pyridine distillate is returned to the pyridine being distd. The operation is continued until the desired degree of dehydration is attained. U. S. 1,416,206 related to the addn. of volatile petroleum oil to facilitate distn. of the  $\text{H}_2\text{O}$ .

**1-Allyl-3,7-dimethylxanthine.** E. PREISWERK. U. S. 1,415,700, May 9. This compd. is prepd. by allowing allyl bromide to act upon the K or Na compd. of 3,7-dimethylxanthine at a temp. of about the b. p. without application of pressure.

**Chlorine derivative of hexamethylenetetramine.** B. BURATTI. U. S. 1,416,606, May 16. A soln. of NaOCl is neutralized by  $\text{H}_3\text{BO}_3$  and a soln. of  $(\text{CH}_3)_6\text{N}_4$  is added to the neutralized hypochlorite soln. in order to produce  $\text{C}_6\text{H}_{12}(\text{NCl})_4$ .

**Metaldehyde.** ELEKTRIZITÄTWERK LONZA. Brit. 176,319, Dec. 5, 1921. The stability under heat of metaldehyde prepd. by the catalytic polymerization of AcH is improved by transforming the residual traces of catalyst into non-catalytic substances or by eliminating any adhering paraldehyde or both. Thus, if  $\text{H}_2\text{SO}_4$  or HCl has been employed as catalyst, a Ba or Ag compd., resp., may be added; adhering paraldehyde may be removed by washing with AcH or by gently heating *in vacuo*.

## 11—BIOLOGICAL CHEMISTRY

PAUL, E. HOWE

A—GENERAL

FRANK P. UNDERHILL

**Periodicity of enzymes: the lipase of the stomach.** E. SLUTTER. *Nederl. Tijdschr. Geneeskunde* 66, 572(1922).—The soln. of the lipase is freshly prepd. from mucous membranes; it is kept in an ice-box during the whole expt. which extends for more than a month. The activity is detd. daily by shaking 5 cc. of the lipase soln. with 5 cc. milk for 24 hrs. at 39° and titrating the free fatty acid formed with 0.1 N alkali. The activity, thus detd., changes irregularly in periods of several days, as illustrated by the following figures: With the same lipase soln. 8.3 cc. were used at first; this figure went down from day to day until after 20 days 3.5 cc. only were used. On the following day the activity suddenly rose, 11.7 cc. being used. Then again it diminished to 6.1 and 6.7, rose again up to 10.7 cc. after 7 days, again went down to 8.7 and after 2 days rose to 10.4 cc., etc. Many more expts. of this kind are described. The activity is also detd. in a slightly acid medium by adding 0.5 cc. 0.1 N HCl; in this case a similar periodicity is observed. S. believes, however, that such variations play no part *in vivo*. R. BRÜTNER

**A study of the decomposition of amygdalin from the point of view of conjugated enzyme reactions.** J. GIAGA. *J. chim. phys.* 19, 77-99(1921).—The decompn. of amygdalin into glucose, BzH, and HCN under the influence of the emulsins of *Helix pomatia* and of the almond is the resultant of at least two successive primary reactions. The glucose is formed relatively more slowly than the BzH and HCN, the two last being produced in equiv. proportions throughout the reaction. The course of the reaction varies with the enzyme used and follows a sort of selective mass action law. Thus, the addition of glucose retards only that part of the reaction which produces it. The same is true of HCN and perhaps of BzH. JAMES A. BRADLEY

**Biochemical synthesis of  $\alpha$ -methyl-d-mannoside.** H. HÉRISSEY. *Bull. soc. chim. biol.* 4, 80-2; *Répert. pharm.* 34, 109-11(1922).—See C. A. 15, 3120. A. T. C.

**Animal light.** PAUL BUCHNER. *Naturwissenschaften* 10, 1-7, 30-4(1922).—A discussion involving no new data. C. C. DAVIS

**The importance of physical chemistry in biology with particular reference to Nernst's theoretical chemistry.** LEON ASHER. *Naturwissenschaften* 10, 193-8(1922).—Stress is laid on the influence of Nernst in the application of phys. chemistry to biology. C. C. DAVIS

**Nature of lipochrome.** C. KREIBICH. *Arch. Derm. Syph.* 127, 762-6(1920); *Physiol. Abstracts* 6, 118.—A description of the staining reactions and properties of the lipid occurring in prostatic secretion, epithelium of seminal vesicles, cardiac muscle, adrenals, and sometimes in the corpus luteum. H. G.

**Note on the work of S. M. Neuschloss: The colloid chemical significance of physiological ionic antagonism and of equilibrated salt solution.** H. HANDOVSKY. *Arch. ges. Physiol. (Pflüger's)* 185, 7-10(1920); *Physiol. Abstracts* 6, 110; cf. C. A. 15, 1734.—H. considers that N.'s balancing ratio of K : Na :: 1 : 20, if not erroneous, is fortuitous, and has no special biological significance in his expts. on lecithin. H. G.

**Solutions deprived of poison through yeasts and other microorganisms, enzymes and protein substances.** T. BOKORNY. *Centr. Bakt. Parasitenk. II Abt.* 52, 26-39(1920); *Physiol. Abstracts* 6, 225.—These organisms and substances bind inorg. and org. acids and bases, forming insol. compds., so that the acids and bases are removed from action in the soln. H. G.

**Decomposition of starch in the presence of saliva ash.** E. BACHRACH. *Compt. rend. soc. biol.* 83, 583 (1920); *Physiol. Abstracts* 6, 113.—There is no action if the ash is kept sterile.

H. G.

**Liquefying and precipitating power of papain.** E. POZERSKI. *Compt. rend. soc. biol.* 83, 657-60 (1920); *Physiol. Abstracts* 6, 226.—Papain, besides its digesting and coagulating components, contains a liquefying component which is destroyed by heating to 90° to 95°. By heating to this temp., papain acquires a pptg. power which it did not previously possess. This power is lost when unheated papain is added to the heated substance.

H. G.

**Action of toluene on dried yeast.** J. GHAJA AND M. DJERMANOVITCH. *Compt. rend. soc. biol.* 83, 1388-9 (1920); *Physiol. Abstracts* 6, 225.—In two cases the fermentative power of dried yeast preps. was much reduced by treatment with toluene. In one case heating the yeast in a powder for 1 hr. at 70° prevented the action of toluene; in the other heating to 45° brought about a gradual lessening of the influence of toluene until after 6 hrs. the influence was nil. Toluene was without influence on yeast from the under part of the first prepn.

H. G.

**Chemical and physical analysis of stimulation phenomenon.** V. GRAPE. *Verh. zool.-bot. Ges. Wien* 70, 1-21 (1920).—The importance of swelling and shrinkage in stimulation is emphasized and discussed.

H. G.

**Melanins.** ANGELO ANGELI AND ANTONIO PIERONI. *Atti accad. Lincei* 30, i, 241-5 (1921).—The authors criticize adversely certain of the results and conclusions of Salkowski (*C. A.* 14, 972). For instance, although melanin may be destroyed completely by boiling alk. permanganate soln., with cold 2% permanganate soln. contg. a few drops of KOH soln. it gives, besides oxalic acid, an acid of the pyrrole or indole series. Further, hypomelanin and sepia-black are readily oxidized in the hot by 30% H<sub>2</sub>O<sub>2</sub> soln. dild. with AcOH giving, on evapn., a sirupy residue which, when heated either alone or in presence of KOH, gives the pine splinter reaction. Salkowski's observation that the melanins yield pyrrole when fused with KOH, the analogies existing between melanins and pyrrole blacks, the property exhibited by pyrrole of furnishing black or brown products when treated either with ordinary oxidizing agents or with oxidases *in vitro* or in living tissue, the fact (cf. *C. A.* 14, 2033) that injections of pyrrole det. in animals, either a melanuria with characters similar to those noted by Eppinger in patients suffering from melanosisarcoma or, if following injection of melanin, the formation of melanotic tumors, render it probable that the color in all these cases is largely due to the one fundamental substance, pyrrole.

J. C. S.

**The action of muscle tissue on fumaric, maleic, glutaric, and malic acids.** H. D. DAXIN. *J. Biol. Chem.* 52, 183-9 (1922).—The enzymes of muscle tissue convert salts of fumaric acid into active malic acid. The levo variety is exclusively formed as opposed to Kinbeck's statement (*C. A.* 8, 2401) that inactive malic acid is produced. Maleic acid under similar conditions gives no active malic acid, while glutaric acid gives a little symmetrical  $\beta$ -hydroxyglutaric acid. On subjecting inactive malic acid to the action of muscle enzymes, the residual malic acid contains an excess of the *d*-component, while some fumaric acid is produced. It would appear that the *l*-component is more readily converted into fumaric acid than the *d*-component. An attempt to effect an asymmetric synthesis of active malic acid by the action of Hg *l*-lactate on maleic acid was unsuccessful. *Bis-phenylhydrazide of inactive malic acid*, from heating 1 mol. of inactive malic acid in 10% aq. soln. with 3 mols. of PhNHNH<sub>2</sub> and 1.5 mols. of AcOH for 3-4 hrs. on a water bath, colorless prisms from hot glacial AcOH by adding an equal vol. of H<sub>2</sub>O, m. 221-4° (uncorr.), is much less sol. in hot alc. than the corresponding deriv. of active malic acid.

A. P. LOTHROP

**Lytropic series and  $\beta$ -oxidation.** K. SPIRO. *Biochem. Z.* 127, 299-311 (1922).—

General discussion of physico-chem. aspects of Hofmeister's work, with special emphasis on the importance of the anions in the lyotropic series. Anions in physiol. fluids do not show the wide variations shown by cations. The predominance of Cl ions influences the physiol. action of the cations through its effect on "hydration" and "solvation" processes—reactions of ions with  $H_2O$  mols. An attempt is made to explain the divergence in the manner of biochem. oxidation of even and uneven C chain compds. by means of expts. with MeOH and EtOH and their respective effects upon pptn. of salts. The greater affinity of MeOH than of EtOH for  $H_2O$  is demonstrated. S. believes that the even and uneven C chain compds. behave physico-chemically as two entirely unrelated series. A detailed discussion of the recent work on  $\beta$ -oxidations follows. Exptl. data will be published later. W. A. FRIEDLÄNDER

Amylocellulose considered as a compound of silicic acid and amylose. G. MARFITANO AND M. CATOIRE. *Compt. rend.* 174, 1128-30(1922).—Both potato and corn starches, when carefully prepd. so as to insure the absence of sand, cellular membranes or other impurities, yield ash contg.  $SiO_2$ . The so-called amylocellulose may be a compd. of the compn.  $[SiO_2(C_6H_{10}O_5)_n]H_2$ . L. W. RIGGS

Remarks on the "elution" of saccharase and maltase from their adsorption compounds. R. WILLSTÄTTER AND R. KUHN. *Z. physiol. Chem.* 116, 53-66(1921).—With yeast invertin adsorbed by  $Al(OH)_3$  it was found that the enzyme could again be obtained in soln. by treatment with phosphate or citrate mixts. + 16% sucrose. Acetate buffers + sucrose were ineffective. Glucose, fructose, maltose and lactose in weak concns. with and without phosphates were ineffective also. Maltase could not be freed with a maltose soln. alone but with a phosphate mixt. + maltose this was accomplished. Egg white soln. alone was ineffective. Phosphate mixts. + weak glycerol solns. made an effective "elutioning" agent. R. L. STEHLÉ

Influence of reaction on the activity of trypsin. W. E. RINGER. *Z. physiol. Chem.* 116, 107-28(1921).—The optimum  $p_H = 11.3$ . The enzyme is stable in fairly strong acid ( $p_H = 3.15$ ) but is rapidly destroyed when  $p_H = 12$ . R. L. S.

Modern ideas respecting acidity and alkalinity. F. W. GAMBLE AND N. EVERS. *Pharm. J.* 108, 175-9; *Chemist and Druggist* 96, 274-7(1922).—A review, with the following summary: "Methods of detg.  $H^+$  concn. distinguish between degree of acidity and amt. of acid present. There is a point of optimum  $H^+$  concn. for biochem. processes, the activities of enzymes, the growth of microorganisms, etc. In dealing with organized material, the  $H^+$  concn. is of great importance. Solns. of pure chem. substances show a definite  $H^+$  concn. which is a valuable indication of purity. The indicators now available allow  $p_H$  detns. to be made with considerable speed and accuracy." S. W.

Enzymes. H. V. EULER AND K. MYRBACK. *Arkiv Kemi Mineral. Geol.* 8, No. 17, 1-15(1922); cf. *C. A.* 14, 2502.—Sucrase prepn. were appreciably purified by treating them with *Bacillus macerans*, takadiastase, and the enzyme prepn. from *Helix pomatia*. Bottom yeast H causes esterification of glucose and of maltose with phosphates, even in the presence of phenol. Alc. fermentation also proceeds in the presence of phenol and of toluene. Although lactose is not fermented by this yeast, it increases the "self-fermentation" of the yeast. J. J. WILLAMAN

Plea for rational interpretation of hydrogen-ion measurements (MOORE) 2. Synthesis of  $\alpha$ -hydroxyisopentacosanic acid and its bearing on the structure of cerebrogenic acid (LEVERNE, TAYLOR) 10. The action of benzoyl peroxide upon cholesterol (WINDAUS, LÜDERS) 10.

GUILLAIN, GEORGES, LAROCHE, GUY, and LECHELLE, P.: La réaction du benzène colloïdal et les réactions colloïdales du liquide céphalo-rachidien. Paris: Masson et Cie. 146 pp. fr. 12.

LEISSGANG, R. Ed.: Beiträge zu einer Kolloidchemie des Lebens (Biologische Diffusionen). 2nd ed. revized. Dresden and Leipzig: Theodor Steinkopf. 39 pp. Medicine. *New Journal*. Quarterly. Baltimore: Williams and Wilkins Co. \$5 per vol. in U. S., Mexico, Cuba; \$5.25, Canada; \$5.50 other countries.

Nouvelle bibliographie des livres de médecine, chirurgie, pharmacie, sciences, 1921-22. Paris: A. Maloine et fils. 64 pp. Fr. 50.

## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

Progress in the investigation and valuation of urine during 1921. F. Utz. *Pharm. Monatshefte* 3, 29-33, 50-4(1922).—A review of the work under the headings: phys. and general chem. procedures, albumin, sugar, acetone and acetoacetic acid, uric acid and urea, dyestuffs, constituents which up to the present time have received no consideration, microscopic examn. W. O. E.

Preparation of gelatin-dye filters for physiological experiments. E. C. PRINGSHEIM. *Ber. bot. Ges.* 37, 184-6(1919); *Physiol. Abstracts* 6, 159.—Directions are given for combining aniline dyes with gelatin, so as to make various light filters by which, alone or in combination, almost any part of the spectrum can be isolated. H. G.

Elementary apparatus for gas analysis and microspirometry in definite gas mixtures and the determination of hemoglobins of earthworms. H. JORDAN AND B. SCHWARZ. *Arch. ges. Physiol. (Pflüger's)* 185, 311-21(1920); *Physiol. Abstracts* 6, 108.—Modification and adaptation of Krogh's micro-gas analysis (capillary) method. Worms survive many hours' exposure to pure CO; on subsequent return to air the O usage is little if at all reduced, although the Hb persists as COHb. But if exposed to low O pressure, previous treatment with CO leads to reduction of O consumption; it is inferred that Hb is only used as an O carrier under conditions of low O environment. H. G.

Examination of blood coagulation. A. FONIO. *Schweiz. med. Wochschr.* 1921, 146-51; *Physiol. Abstracts* 6, 187.—Description of a method by a new simple app., by which in 20 cc. blood the coagulation time, the coagulation valency (*i. e.*, the capability to overcome a measured inhibition of coagulation by  $MgSO_4$ ), the elasticity, *d.*, and contractility of the clot are ascertained. This combined method of investigation is regarded as of great practical and prognostic importance. H. G.

The colorimetric estimation of tyrosine and the phenolic number of proteins. PIERRE THOMAS. *Bull. soc. chim. biol.* 3, 197-216(1921).—In the estn. of tyrosine in proteins by the colorimetric method of Folin and Denis (*C. A.* 6, 3433) the presence of tryptophan, skatole, indole, and reducing reagents vitiates the results; hence the method is untrustworthy and must be rejected (*cf.* Abderhalden and Fuchs, *C. A.* 7, 2049; Folin and Denis, *C. A.* 7, 2406). T. suggests the characterization of proteins by means of their phenolic numbers, the latter being defined as the numbers, calcd. in percentages of tyrosine, which represent the phenolic constituents of the hydrolyzates. For the estn. of the phenolic number a weighed portion of the protein is hydrolyzed with 25%  $H_2SO_4$ , filtered from humin, neutralized with  $Ba(OH)_2$ , acidified with  $HNO_3$  and filtered. Just sufficient  $Hg(NO_3)_2$  is then added to an aliquot part of the filtrate to ppt. the tryptophan. After decolorization, if necessary, by addn. of a small quantity of animal charcoal, the color produced by the addn. of 2 cc. of Millon's reagent to 10 cc. of the filtered soln. is compared with a tyrosine standard. The results of a number of estms. are given. J. C. S.

Micro-estimation of carbon monoxide in blood. MAURICE NICLOUX. *Bull. soc. chim. biol.* 3, 286-96(1921).—A micro-modification of N.'s method (*C. A.* 15, 2860

for the estn. of CO in blood is described; 2 to 5 cc. of blood are used for an estn. It is claimed that the method is simple and accurate to within 2%. Notes are given on the application of the method to the estn. of the capacity of the blood for absorbing CO, and of the amt. of the latter present in blood in cases of poisoning. J. C. S.

Urobilin and stercobilin (in the urine) of infants. MARCHI, BRULÉ AND H. GARRAN. *Compt. rend. soc. biol.* 84, 482-3 (1921).—In the examn. of urines, when urobilinogen is changed into urobilin the oxidation is generally carried too far, so that urobilin is decomposed. The authors recommend the addn. to 10 cc. of urine of a small quantity of Zn acetate and an equal vol. of 95% alc. The liquid is filtered after half an hr. and tested by means of fluorescence. Urine of newly born infants, of high density, contains much urobilin; in urine of lower density urobilin is detected with difficulty. There is no correlation between the urobilin content of the urine and the appearance of stercobilin. Urobilin may be found considerably before stercobilin appears. Urobilin in the newly born is formed from the blood pigment and is due to hyperhemolysis. These facts contradict the "enterohepatic" theory of urobilinuria. J. C. S.

Comparison of methods for estimation of uric acid in blood. PIETRO BIERI. *Riv. osp.* 11, 29-40.—The methods of Ludwig-Salkowski, Schittenhelm-Schneller, Kowarski (piperidine), and Aufrecht (hydroxyl estn. of  $\text{NH}_4$  urate) for the estn. of uric acid in blood were compared in cases of pathological bloods. The agreement was unsatisfactory, but the first two gave the most concordant results. The second method would appear to be the most trustworthy. A modification of the Kowarski method (pptn. of the proteins by sulfosalicylic acid, transformation by means of  $\text{NH}_4\text{Cl}$  into ammonium urate, and, after washing with EtOH-acetone, estn. of the  $\text{NH}_3$ ) gave passable results, but was less accurate than the methods first named. J. C. S.

Rapid estimation of urea in urine, blood, and other physiological fluids. H. STROHMANN AND S. FLINTZER. *Zentr. inn. Med.* 42, 545-62 (1921).—An examn. of the methods of Folin and his co-workers (*C. A.* 13, 2541). Difficulties in the hydrolysis by means of urcase may be avoided by using smaller amts. of material (= about 0.2 g. of urea N) and working at greater dilns. On account of the errors consequent on the small amts. of N to be estd., the older method of Marshall (*C. A.* 7, 2048-9) was tried. It gave more concordant results but demanded longer time. Using 10 cc. of blood filtrate (instead of 5 cc. as in Folin's method), the liquid may be nesslerized directly after hydrolysis if the same amt. of ferment ext. is added to the liquid used for comparison. The method to be adopted for the preliminary removal of protein will vary according to the liquid under examn. and the amt. of protein present. J. C. S.

A possible source of error in the Bell-Doisy method for the determination of phosphates in blood plasma. W. DENIS AND L. VON MEYSENBUG. *J. Biol. Chem.* 52, 1-3 (1922).—The Bell and Doisy method (*C. A.* 15, 3685) is reliable for the detn. of inorg. phosphates in serum but excess of oxalate or citrate in plasma prevents the color development. Whenever possible, therefore, the detn. should be made on serum. Where plasma must be used the amt. of  $\text{K}_2\text{C}_2\text{O}_4$  should be restricted to 25 mg. and of Na citrate to 20 mg. per 10 cc. of blood; in addn. 2 cc. of molybdate reagent and 2 cc. of hydroquinone soln. of double strength (40 g. per l.) should be added to 10 cc. of the  $\text{CCl}_3\text{CO}_2\text{H}$  filtrate (diln. 1:10). Results under these conditions with plasmas are identical with those obtained on the serum of the same individual. The modification has been applied to both horse and human adult plasmas. A. P. LOTHROP.

A method for the quantitative estimation of minute amounts of gaseous oxygen and its application to respiratory air. H. M. SHEAFF. *J. Biol. Chem.* 52, 35-49 (1922).—"A microchem. method for the estn. of  $\text{O}_2$  has been devised depending upon the colorimetric estn. of nitrite formed in the interaction of  $\text{O}_2$  and NO in the presence of NaOH

**soln.**—This method is sufficiently delicate for measuring amts. of  $O_2$  of the order of magnitude  $1 \times 10^{-7}$  g., or less than 0.1 cu. mm. of the gas. Application of the method has been made to the *micro-respiration of frog sciatic nerves* and it has been found that from 0.424 to  $0.76 \times 10^{-4}$  g. of  $O_2$  is used by 10 mg. of nerve per 10 min. in the 'resting' state and from 1.32 to  $1.51 \times 10^{-4}$  g. when stimulated by weak induced shocks." It was not possible at the time the detns. were made to make  $O_2$  and  $CO_2$  estns. simultaneously for the purpose of checking gaseous intake against gaseous output.

A. P. LOTHROP

**The differential precipitation of the proteins of colostrum and a method for the determination of the proteins in colostrum.** PAUL E. HOWE. *J. Biol. Chem.* 52, 51-68(1922); cf. *C. A.* 16, 729.— $Na_2SO_4$  solns. at  $37^\circ$  may be used to sep. the proteins of colostrum and the process is capable of quant. application. The material sep'd. at the various concns. of  $Na_2SO_4$  in the proportion of 31 : 1 is considered to consist of the following proteins or mixts. of proteins: (a) at 14.0-14.2%, euglobulin; (b) at 18.0-18.4%, euglobulin, pseudoglobulin I, and casein; and (c) at 21-22%, euglobulin, pseudoglobulin I and II, and casein. The casein is ppt'd. by the addn. of AcOH to the filtrate from the  $Na_2SO_4$  pptn. at the euglobulin crit. zone. The non-protein N is det'd. as usual after removal of the proteins with 5%  $CCl_3CO_2H$ . The filtrate N is det'd. in each case and the amts. of the different types of protein N are calcd. by making the proper subtractions. The euglobulin and pseudoglobulins I and II of colostrum have the same characteristics as the similar proteins found in blood (*C. A.* 16, 741).

A. P. LOTHROP

**A method of quantitative determination of trypsin. A modification of Gross' method.** SOTARO KAI. *J. Biol. Chem.* 52, 133-6(1922).—*Method.*—Transfer 25 cc. of the stock alk. casein soln. to each of two 50 cc. flasks and warm to  $40^\circ$  in a thermostat. To one flask add 1 cc. of standard trypsin soln. and to the other 1 cc. of the unknown, noting the time of the addition. Mix well and replace in the thermostat. At 5-10 min. intervals pipet off 2 cc. from each flask and mix with 1 cc. of NaOH-AcOH mixt. in a test-tube. Note the time at which the digest fails to give any white ppt. The standard will usually require 15-20 min. The rate of digestion is simply proportional to the amt. of trypsin and the time of digestion is, therefore, inversely proportional to the concn. of the enzyme. *Reagents: Alk. casein soln.*—Dissolve 1 g. of pure casein in 15 cc. of 0.1 N NaOH, add 400 cc. of dist'd.  $H_2O$  and titrate 10 cc. of this soln. until just colorless to phenolphthalein, using 0.01 N HCl. Add a corresponding amt. of the acid to the remainder of the casein soln. and make up to 500 cc. (0.2% casein soln.). *NaOH-AcOH mixt.*—Mix 17.2 cc. of N NaOH and 33.7 cc. of N AcOH and make up to 100 cc. *Standard trypsin soln.*—Dissolve 0.01 g. of good com. trypsin in 10 cc. of  $H_2O$ , filter and preserve with  $C_2H_5$ .

A. P. LOTHROP

**Determination of fatty acids (and cholesterol) in small amounts of blood plasma.** W. R. BLOOR, K. F. PELKAN AND D. M. ALLEN. *J. Biol. Chem.* 52, 191-205(1922).—Bloor's method (*C. A.* 8, 1970; 10, 1656) for the detn. of fatty acids in blood plasma has been so modified that the fatty acids are det'd. separately instead of being calcd. from the difference between cholesterol and fatty acid (total fat) and cholesterol (det'd. separately in another sample of ext.). The figures obtained by the original method were apt to be quite incorrect. The following is an outline of the new method: "The lipid substances may be satisfactorily ext'd. from blood plasma by treatment with excess of hot alc.- $Et_2O$ . In these exts. the fatty acid constituents of the lipids may be sep'd. from the cholesterol by sapon. of the ext. and extn. of the sapon. residue with cold  $CHCl_3$ , which exts. the cholesterol, leaving the fatty acids (soaps) behind. These may be ext'd. from the residue with hot alc. Detn. of the cholesterol is made on the  $CHCl_3$  ext. after suitable concn. by the Liebermann-Burchard reaction. Detn. of the fatty



acid is made on the alc. ext. nephelometrically, by the acid pptn. method.

A. P. LOTHROP

A colorimetric method for the determination of small amounts of magnesium. F. S. HAMMETT AND E. T. ADAMS. *J. Biol. Chem.* 52, 211-15(1922).—The method is a combination of the technic of Kramer and Tisdall (*C. A.* 15, 3859) and Bell and Doisy (*C. A.* 15, 3685) and is applicable for the estn. of small amts. of Mg in urine, blood and tissue exts. or incinerations. The results have a tendency to be somewhat low owing either to incomplete pptn. or to soln. during washing but with care the loss can be held to within about 3%. Its main advantage lies in the colorimetric comparisons which are exact and clean-cut. *Method on solns. of bone ash.*—Pipet 5 or 10 cc. (depending on the wt. of the bone ash and the diln. of the soln. made therefrom) of the clear supernatant liquid from the pptn. of Ca according to Kramer and Tisdall into a 30 cc. beaker, add, drop by drop, 1 cc. of  $(\text{NH}_4)_2\text{HPO}_4$  soln. and then 2 cc. of  $\text{NH}_4\text{OH}$  similarly. Allow to stand overnight, filter through asbestos in a 27 mm. Gooch crucible with mild suction, wash 10 times with 5 cc. portions of 10%  $\text{NH}_4\text{OH}$  and twice with 90% alc. made alk. with  $\text{NH}_4\text{OH}$ . Replace the crucible in the beaker and dry at  $80^\circ$  for a few min. Add 10 cc. of 0.01 N HCl to the contents of the crucible and allow to stand for 3 hrs. at room temp. (or use 10 cc. of 0.1 N HCl with 1 hr. standing). Transfer the contents of the crucible and beaker to a test-tube and sep. the asbestos by centrifuging. Pipet 5 cc. of the supernatant fluid into a 25 cc. volumetric flask. In a second flask place 5 cc. of a standard  $\text{KH}_2\text{PO}_4$  soln. contg. 0.05 mg. of P. To both flasks add 5 cc. of phosphate-free  $\text{H}_2\text{O}$ , 1 cc. of molybdate soln., 2 cc. of the hydroquinone soln. and after 5 min. 10 cc. of the carbonate-sulfite soln. of Bell and Doisy. Make up to the mark and after 5-10 min. compare in a colorimeter. The amt. of P found in the test soln. multiplied by  $0.7835 \times 2$  gives the amt. of Mg in the sample removed from the supernatant liquid from the Ca detn.

A. P. LOTHROP

A method for the determination of small amounts of lactic acid. S. W. CLAUSSEN. *J. Biol. Chem.* 52, 263-80(1922).—Methods are described for the detn. of lactic acid in urine and blood giving a provisional normal figure of 5-13 mg. per 100 cc. for the former and 15-32 mg. per 100 cc. for the latter. The methods are based on the conversion of lactic acid into  $\text{MeCHO}$  by the action of concd.  $\text{H}_2\text{SO}_4$  at  $140^\circ$ , the aeration of the  $\text{MeCHO}$  into an excess of  $\text{NaHSO}_3$  and a final titration of the bound sulfite with standard I soln. The methods are not specific for lactic acid but det. a group of substances which yield bisulfite-binding compds. Efforts have been made to remove from blood and urine as many as possible of those compds. known to interfere, such as glucose, phenols, etc.

A. P. LOTHROP

Studies on uric acid. I. Examination of the variables in the Folin and Wu uric acid method. GEO. W. PUCHER. *J. Biol. Chem.* 52, 317-27(1922).—The Folin-Wu method (*C. A.* 13, 2541) is the most rapid and accurate for the detn. of uric acid in small amts. of blood but when uric acid is added to sheep blood the recovery is consistently only about 75%. The loss is due to mech. retention or absorption by the pptd. proteins. The uric acid must be pptd. in neutral soln. by Ag lactate or consistent quant. results cannot be obtained. Temps. below  $20^\circ$  have no effect on the soly. of Ag urate. Within the accuracy of the colorimeter (2-3%) the readings are proportional to the amt. of uric acid present without applying any corrections. When  $\text{CCl}_3\text{CO}_2\text{H}$  is used as a protein precipitant only 50% recovery of uric acid is obtained; ordinarily the uric acid N is such a small fraction of the total N that its effect is almost negligible but this is frequently not the case in many pathological samples of blood. II. A modification of the Folin and Wu uric acid method. *Ibid* 329-34.—If the soln. contg. the pptd. blood proteins is heated before filtration, 93% of the uric acid can be obtained and the method is much more rapid owing to the increased speed of filtration. Measure 5 cc.

of oxalated (excess  $K_2C_2O_4$  must be avoided) whole blood with a Folin pipet into a 125 cc. long narrow-necked Florence flask. Take with 35 cc. of  $H_2O$ , add 5 cc. of 10%  $Na_2WO_4$  soln. and 5 cc. of  $\frac{1}{2}$  N  $H_2SO_4$ . Shake vigorously and after allowing the mixt. to stand 5–10 min. (the color must be a chocolate brown) immerse the flask in a boiling water bath (95–98°) for 5–8 min. Remove, shake gently and filter. After the filtrate has cooled to room temp. measure 20 cc. into a 50 cc. centrifuge tube, add 0.5 cc. of dil.  $NH_4OH$  (14 cc. of concd.  $NH_4OH$  dild. to 500 cc.) and then with stirring 3 cc. of a 5% soln. of Ag lactate in 5% lactic acid. Allow to stand 10–15 min., centrifuge for 2 min. and carefully pour off the clear supernatant liquid. Thoroughly triturate the residue with 2 cc. of a 10% NaCl soln. in 0.1 N HCl, taking great care that all particles are loosened from the bottom of the centrifuge tube and brought into intimate contact with the acid. Wash the stirring rod and sides of the tube with 10 cc. of  $H_2O$  and centrifuge again. Pour the clear liquid into a 25 cc. volumetric flask. Pipet 1 cc. of the standard uric acid soln. (prepd. according to the directions of Folin) into a 50 cc. volumetric flask and wash down the sides with 4 cc. of the 0.1 N HCl and 20 cc. of  $H_2O$ . With shaking add to the standard 10 cc. and to the unknown 5 cc. of a combined Na sulfite-carbonate-cyanide reagent (20 g. of anhyd.  $Na_2SO_3$ , 120 g. of anhyd.  $Na_2CO_3$  and 5 g. of NaCN (100% NaCN basis) dissolved in warm  $H_2O$  and made up to 1 l.). Allow to stand for at least 10 min. and then add to the standard 1 cc. and to the unknown 0.5 cc. of the uric acid reagent of Folin and Denis. (Heat 100 g. of  $Na_2WO_4$ , 80 cc. of  $H_3PO_4$  and 70 cc. of  $H_2O$  under reflux for 2 hrs. and dil. to 1 l.) Shake, allow to stand 3–5 min., dil. to the mark and read in the colorimeter. Readings are best made in a dark room and the av. of 6–10 readings should be taken as the correct value. Before use the  $Na_2WO_4$  and  $\frac{1}{2}$  N  $H_2SO_4$  should be titrated against each other with methyl orange as indicator; 5 cc. of the  $Na_2WO_4$  should be equiv. to about 3.0 to 3.3 cc. of the  $H_2SO_4$  which will insure an almost neutral blood filtrate (0.005 to 0.002 N). A slight opalescence or turbidity in the hot blood filtrate does not interfere with the detn.; the final soln. will be water-white.

A. P. LOTHROP

The reaction of tissues to bromothymol blue. A method for determining death. SILVIO REBELLO. *Compt. rend. soc. biol.* 86, 615–8(1922).

S. MORGULIS

The determination of uric acid in urine by means of Folin and Denis' phosphotungstic reagent. M. THIÉRY. *Société de pharmacie de Paris*, Nov. 9, 1921; *Ann. chim. anal. chim. appl.* 4, 146–7(1922); *J. pharm. chim.* 25, 87–92; *Reper. pharm.* 34, 111–12(1922).

A. P.-C.

Determination of uric acid in blood. CH. O. GUILLAUMIN. *J. pharm. chim.* 25, 5–15(1922).—See C. A. 16, 1794.

S. WALDBOTT

Detection of bismuth in urine. PIERRE AUBRY. *J. pharm. chim.* 25, 15–8(1922).—In the Bi treatment of syphilis (C. A. 15, 3145), a black ppt. of  $Bi_2S_3$  sometimes forms in the urine on standing. A's iodoquinic reagent (quinine sulfate 1 g.,  $H_2SO_4$  3 or 4 drops, KI 2 g.,  $H_2O$  to make 100 cc.; cf. Léger's cinchonine reagent) detects Bi in all cases when administered, by an orange-red ppt. obtained with the urine after evapn., ashing and soln. in dil.  $HNO_3$ . The color is still visible in a diln. of 1 : 600,000 of  $Bi_2O_3$ . A direct colorimetric detn. was not successful.

S. WALDBOTT

Determination of calcium in the blood. P. MAZZOCCO. *Compt. rend. soc. biol.* 1921, 689; *J. pharm. chim.* 25, 33–4, 42(1922).—To at least 1 cc. of serum add an equal vol. of 15%  $CCl_3CO_2H$  (A); after 10 min. filter, remove and stir the ppt. with 10 cc. of 5% A, put through the same filter and wash out. Ppt. the Ca with 2 cc. of 2.5%  $(NH_4)_2C_2O_4$  from weak  $NH_4OH$  soln., boil for 10 min.; after 6 hrs. centrifuge, wash with little  $H_2O$ , add 4 cc. of 5%  $H_2SO_4$  and titrate at 60° with  $KMnO_4$  (1 cc. = 0.00014 g. Ca). To prep. this  $KMnO_4$  dissolve 0.25 g. in 1 l. of  $H_2O$ , boil at reflux for 36 hrs., filter through calcined asbestos, make up to 1 l. Titrate every 3 days with soln. of 1.101

g.  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in 1000 cc. The soln. is stable for 2 months. In man, total blood contains 7.15 mg. Ca per 100 cc., most of it in the liquid part. S. W.

Simplified determination of non-protein nitrogen of blood. A. GRIGAUT and J. THIRY. *Compt. rend. soc. biol.* 85, 812(1921); *J. pharm. chim.* 25, 34-6(1922).—Remove albumin from serum, total blood or globules with an equal vol. of 20%  $\text{CCl}_4 \cdot \text{CO}_2\text{H}$ . To 2 cc. of the filtrate, add in a pyrex tube 1 cc. of a mixt. of 100 cc.  $\text{H}_2\text{SO}_4$  of 66° Bé. and 100 cc. of 0.5%  $\text{CuSO}_4$  and heat until the  $\text{H}_2\text{O}$  and then the C are removed. Cool, and dissolve in  $\text{H}_2\text{O}$  to 80 cc. To 25 cc. of a  $(\text{NH}_4)_2\text{SO}_4$  standard soln. (1 cc. = 0.01 mg. N; dil. to 1 l. 10 cc. of a soln. of 4.716 g.  $(\text{NH}_4)_2\text{SO}_4$  in 1 l. of 0.2 N  $\text{H}_2\text{SO}_4$ ) add 1 cc. of the  $\text{H}_2\text{SO}_4 \cdot \text{CuSO}_4$  soln. and again fill up to 80 cc. Nesslerize both solns. by filling up to 100 cc. and compare tints in a Duboseq colorimeter. Equality of tint in both solns. corresponds to the normal 0.25 g. non-protein N per l. of serum.

S. WALDBOTT

A mercury or water ureometer for the determination of urea in urine or blood. R. CLOONE. *J. pharm. chim.* 25, 99-100(1922).—The instrument is of the Yvon, Grimbert or Ambard type.

S. WALDBOTT

The colorimetric determination of hydrogen-ion concentration in biological liquids. CH. O. GUILLAUMIN. *J. pharm. chim.* 25, 173-80, 221-8, 306-13(1922).—A review of the method and its application to the detn. of  $p_H$  in culture media, blood, cerebrospinal fluid, urine, gastric juice, and milk.

S. WALDBOTT

New stalagmometer or guttometer (ESCHBAUM) 1. Some new color reactions of cholesterol (KARLENBERG) 10.

## C—BACTERIOLOGY

A. K. BALLS

Conidia-forming substances of the fungi. F. BOAS. *Ber. bot. Ges.* 37, 57-62 (1919); *Physiol. Abstracts* 6, 161-2.—Conidia formation in *Aspergillus niger* is largely dependent on the nature of the substratum. Maltose and raffinose give conidia in large quantities, dextrose, levulose and saccharose much less. With nitrogenous substances like acetamide, glycine, urea, and asparagine the effect on conidia production appears to vary directly with the degree of dissociation of the substance.

H. G.

The action of oscillating currents upon bacteria and protozoa particularly in solutions of iodides. PHILIPP AND CARTHAUS. *Z. physik. diätet. Therap.* 25, 534-8(1921).—Bacteria of every variety, including the branching forms, may be killed by a combination of NaI soln. and oscillating current.

E. B. F.

Formation of organic acids by *Aspergillus niger*. F. ELFVING. *Översigt Finnska Vetenskaps-Soc. Förh. Math. Naturw.* 1918-19 [publ. 1920] 61, No. 15, 23 pp.; *Physiol. Abstracts* 6, 162.—This fungus did not develop on pure solns. of glucose or sucrose, but if a sheet of the fungus is presented with such a soln., and if free O is present, much oxalic acid is formed which is later in part used again. The fungus behaves similarly on solns. of lactose, mannitol, inulin, dextrin, glycerol, peptone, and asparagine. The acid formation is increased by rendering the soln. alk., and it is significantly greater at a higher than at a lower temp. On a complete nutrient soln. with  $\text{NH}_4\text{Cl}$  or  $(\text{NH}_4)_2\text{SO}_4$  as source of N, oxalic acid does not collect.  $\text{NH}_4$  salts of different org. acids do not act in this way. Citric acid is also formed, often in greater quantity than oxalic acid; it is used up before the latter. The power of acid accumulation varies with the race of the fungus; there are some which only accumulate citric acid. Ca salts hinder the formation of oxalic acid. The acids are not formed directly from sugar but by the breaking down of intermediate complex compds.

H. G.

Acid strength by fat-secreting microorganisms. P. LINDNER. *Wochsche. Bros.* 37,

251-7(1920); *Physiol. Abstracts* 6, 224.—Methods are described for differentiating in the cells of fat-secreting microorganisms between esters, fatty acids, and neutral fats.

H. G.

**Endo's reaction.** Contribution to the study of *Bacillus coli*. O. FERNANDEZ AND T. GARMENDIA. *Anales soc. españ. fis. quim.* 19, 313-9(1921).—Various modifications of Endo's culture were inoculated with *B. coli* and the amt. of AcH formed quant. detd. No effect was produced by increasing the  $\text{Na}_2\text{SO}_4$  or replacing it by  $\text{Na}_2\text{HPO}_4$ , nor by increasing the lactose or replacing it by sucrose or glucose; substitution of mannitose for lactose decreased the AcH to traces only. The addition of amino acids, glycine or alanine, increased the amt. of AcH considerably.

L. E. G.

**Adaptation and selection of the lactic acid enzyme in poisonous media.** CH. RICHERT, H. CARDOT AND E. BACHRACH. *J. physiol. path. gén.* 19, 466-79(1921); cf. *C. A.* 16, 732.—By following the growth and acid production of lactic acid bacteria in normal media and in media to which various toxic compds. were added, it was found that apparently the resistance of individual microorganisms is variable, even when they are derived from one cell. On the other hand the lactic bacillus acquires a tolerance to certain poisons, especially  $\text{TINO}_3$ . The phenomenon is irregular in its course. Tolerance to  $\text{HgCl}_2$  is apparently impossible.

F. S. HAMMETT

**Presence of calcium thiosulfate in *Achromatium oxaliferum*, Schew.** GERMAINE HANNÉVART. *Bull. acad. roy. Belg.* 1920, 600-5.—In the vacuoles of *Achromatium oxaliferum*, Schew., S granules occur accompanied by  $\text{CaS}_2\text{O}_4$ . The vacuolar substance disappears at 50-60° and seps. In pure water, the bacteria quickly lose all S by change to  $\text{H}_2\text{S}$ .

J. C. S.

**Oxidation of glycerol by *Bacillus subtilis*.** E. AUBEL. *Compt. rend. soc. biol.* 84, 574-6(1921); cf. *C. A.* 15, 107.—Ten-day cultures of *B. subtilis* in nutrient solns. contg. glycerol were extd. with ether and the residue was treated with  $\text{NaHSO}_4$ . The H sulfite compd. was decomposed by  $\text{H}_2\text{SO}_4$ , dissolved in ether, and again evapd. The residue was dissolved in water and kept for 24 hrs. at the ordinary temp. after addn. of phenylhydrazine and lactic acid. A red substance, m. p. 190°, believed to be the phenylhydrazone of pyruvic acid, was obtained. With the distillate from the culture soln., an osazone of m. p. 240° was obtained, which had the characters of the osazone of acetyl-methylcarbinol. In the residue from distn., traces are found of a substance optically inactive but reducing Fehling soln. weakly. After addn. of  $\text{H}_2\text{SO}_4$ , a distillate is obtained which gives with codeine the coloration characteristic for methylglyoxal. The substance is therefore probably dihydroxyacetone. Pyruvic acid plays an important part in biological syntheses. Cultures develop better in media contg. pyruvic acid than in those contg. dextrose. The successive steps in the oxidation of glycerol are probably glycerol  $\rightarrow$  dihydroxyacetone  $\rightarrow$  methylglyoxal  $\rightarrow$  pyruvic acid.

J. C. S.

**A study of ammonia production by a certain strain of avirulent human tubercle bacillus.** A. W. BOSWORTH, M. G. ELKINS AND MARGUERITE E. BLANCHARD. *J. Infect. Diseases* 30, 357-62(1922).—A study of the N metabolism, during 6 wks., of a certain avirulent culture of tubercle bacilli revealed the fact that there is a continuous production of  $\text{NH}_3$  in plain, dextrose, mannitol and glycerol broths. Over 30% of the N originally present in the medium may be converted into  $\text{NH}_3$ . The  $\text{NH}_3$  produced is partly retained in the medium but the greater part is lost through volatilization. The loss of  $\text{NH}_3$  is coincident with an alk. reaction of the medium. There was no recession in the production of  $\text{NH}_3$  by the organisms during the 6 wks. of the expt. The "waxing and waning" of  $\text{NH}_3$  as noticed by Kendall, Day and Walker (*C. A.* 14, 754) is due to a continuous production of  $\text{NH}_3$  by the organism, and a loss of  $\text{NH}_3$  from the medium into the air by volatilization. So long as the medium remains acid both the total N and the  $\text{NH}_3$  contents of the broth show no decrease. When the broth becomes alk. both

the total N and  $\text{NH}_4$  contents show a decrease. utilized by the tubercle bacilli the amt. is extremely small in comparison with the amt. lost by volatilization.

JULIAN H. LEWIS

Cultural requirements of bacteria. I and II. J. H. MUELLER. *J. Bact.* 7, 309-38 (1922).—The necessity of a non-protein substance is shown by the failure of a trypsin digest of purified casein to support growth while that of impure casein is satisfactory. Peptone-free beef heart infusion plus glucose and inorg. salts is a satisfactory medium for the hemolytic streptococcus. Short boiling of the heart infusion with 2% wood charcoal removes some component which renders it unsuitable for the streptococcus. Such an inactive infusion may be reactivated by the addition of small amts. of peptone or acid hydrolyzate of certain proteins such as casein and edestin. Acid hydrolyzates of wool, silk and wheat gluten are not suitable. The activating material may be pptd. from hydrolyzates of casein by  $\text{HgSO}_4$ . It may be sepd. into two fractions, active only when mixed together, by means of fractional pptn. of the first ppt. by  $\text{HgSO}_4$ , or pptn. by  $\text{Ag}_2\text{SO}_4$  and  $\text{Ba}(\text{OH})_2$ . So far as has been learned, known amino acids will function in place of neither of these fractions. The  $\text{Ag}_2\text{SO}_4$  ppt. does not depend for its activity on the pigment. It escapes pptn. by phosphotungstic acid under certain conditions but is readily destroyed by this reagent. The  $\text{Ag}_2\text{SO}_4$  filtrate contains a considerable amt. of a new S-contg. amino acid, the relation of which to the active constituent has not yet been demonstrated.

JOHN T. MEYERS

The thermophilic bacteria. I. Aerobic thermophilic bacteria from water. L. E. MORRISON AND F. W. TANNER. *J. Bact.* 7, 343-66 (1922).—All the thermophilic bacteria studied were proteolytic, which makes them of importance in food preservation. Their ability to grow at high temps. may be due to a particular property of the protoplasm, possibly water content. A long bibliography is appended.

JOHN T. MEYERS

Change of acid agglutination optimum as index of bacterial mutation. P. H. DE KRUIF. *J. General Physiol.* 4, 387-93 (1922).—The bacillus of rabbit septicemia, type D, has an agglutination optimum of  $p_H$  3.5 to 3.0; that of the mutant, type G, lies between  $p_H$  4.7 and 3.8. The optimum for D is very const.; for G it is slightly less const. After passage through 3 rabbits, G required still less acid to produce agglutination. These differences imply a fundamental difference in the chem. constitution of these organisms. The mechanism of granular growth of rabbit septicemia bacillus type G. *Ibid.* 395-402.—The optimum for acid agglutination of types D and G depends on the nature of the buffer mixt. Glycocoll-HCl buffers cause complete flocculation at  $p_H$  2.7-2.4, while Na lactate-lactic acid buffers show little or no flocculation at this range. Beef infusion broadens the acid agglutination optimum of types D and G in the direction of lower H-ion concn. It does not have the power of agglutination but seems to increase the sedimentation in the presence of H-ions. Fairchild's peptone shifts the agglutination optimum of types D and G in the direction of higher H-ion concn. Large concns. of peptone have an inhibiting effect on the agglutination of D at its optimum  $p_H$  zone.

CHAS. H. RICHARDSON

Methods for the isolation of filter-passing anaerobic organisms from human nasopharyngeal secretions. P. K. OLITSKY AND F. L. GATES. *J. Am. Med. Assoc.* 78, 1020-2 (1922).—Detailed methods of isolating and cultivating *Bacterium pneumosinies*.

L. W. RIGGS

Action of pyocyanic bacillus on glucose and levulose. E. AUBEL. *Compt. rend.* 173, 1493-5 (1921).—The technic of a preceding study was followed (cf. *C. A.* 16, 273). The medium used contained  $\text{NH}_4\text{Cl}$  2 g., hexose 5,  $\text{KH}_2\text{PO}_4$  1,  $\text{MgSO}_4$  1,  $\text{H}_2\text{O}$  1000. With glucose no fixed acids were detected.  $\text{HCOOH}$ ,  $\text{AcOH}$ , and  $\text{EtOH}$  were present. With levulose the same substances were present and in addition lactic acid. The degradation

of the 2 hexoses is represented: hexose  $\rightarrow$  methylglyoxal  $\rightarrow$  pyruvic acid  $\rightarrow$  acetaldehyde  $\rightarrow$  (EtOH and AcOH)  $\xrightarrow{\quad}$  AcOH and HCHO  $\xrightarrow{\text{O}}$  HCOOH.

L. W. RIGGS

**Influence of presence of dust on growth in vitro of certain microorganisms.** E. H. CLUVER AND A. MAVROGORDAYO. *Med. J. S. Africa*, Johannesburg 17, 26(1921); *J. Am. Med. Assoc.* 77, 1687.—The authors endeavored to ascertain whether the presence in culture mediums of various insol. and chem. inactive dusts appreciably influences growth of certain organisms. The dusts employed were powdered quartzite, coal, wood charcoal and charcoal from sugar. *B. pyocyaneus*, streptococcus and *B. tuberculosis* (human) grew more rapidly and more abundantly in the dusted than in the dust-free mediums. No appreciable difference was observed between the different kinds of dust. With pneumococcus the same general effect was observed but quartzite dust appeared to augment the growth less than the other dusts. L. W. RIGGS

**Water-soluble B and bios in yeast growth.** E. I. FULMER AND V. E. NELSON. *J. Biol. Chem.* 51, 77-81(1922); cf. *C. A.* 15, 604.—Data are presented which verify previous work to the effect that 95% alc. ext. of alfalfa does not improve medium F (which promotes the growth of yeast without vitamin) for the growth of yeast. The failure of Eddy, Heft, Stevenson, and Johnson (*C. A.* 15, 3306) to corroborate the results of F. and N. might have been due either to the use of temps. varying between 30° and 35° when 30° and that temp. only is optimum for medium F, or to the use of an aq. or 40% alc. ext. of alfalfa instead of a 95% alc. ext. The addition of an aq. ext. does stimulate yeast growth in medium F and evidently contains, along with H<sub>2</sub>O-sol. B and other materials, bios, the yeast growth stimulant; a 95% alc. ext. contains H<sub>2</sub>O-sol. B but not bios. A reply to Fulmer, Nelson, and Sherwood concerning medium F. WALTER H. EDDY, H. L. HEFT, AND H. C. STEVENSON. *Ibid* 83-5.—Stimulation of yeast growth has been obtained in repeating expts. of F. and N. with a 95% alc. ext. at 30°. The stimulation is not as great as with an aq. ext., indicating that alc. is a poorer extractant of vitamin B than H<sub>2</sub>O as various investigators have pointed out. The results obtained which showed greatest stimulation were with concns. much greater than those used by F. and N., which facts combined with the greater accuracy of the Funk method of measuring yeast growth which was employed, could easily account for their failure to observe stimulation with the alc. ext. The results "clearly indicate the need of very careful study to evaluate all the factors concerned in the response of the yeast cell and if these factors can be evaluated it is believed that it may result in showing that vitamin B plays a part in the action and in perfecting the test for the detection of that factor." The test as at present employed is not an accurate measure of vitamin B content. A. P. LOTHROP

**Nitrogen nutrition of yeast.** F. K. SWOBODA. *J. Biol. Chem.* 52, 91-109(1922).—In previous studies on the N nutrition of yeast the growth-stimulating vitamin factor ("bios" of Wilder) has in no case been properly controlled; accordingly these studies have been carried out with a const. concn. of vitamin (obtained from yeast by extn. with 90% alc.) in media contg. as N sources variously hydrolyzed protein with and without the addition of certain amino acids or several other nitrogenous compds. in various concns. Asparagine is a particularly good form of N for yeast growth but the growth is better if (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is also present. Similar results are obtained with succinamide, succinimide and aspartic acid. The yeast obtains its N mainly from the  $\alpha$ -amino group and only slightly affects the amide group of the asparagine when grown in an asparagine-contg. medium practically free from NH<sub>4</sub>. Mild acid hydrolysis of edestin improves it as a yeast nutrient up to a certain point, after which its efficiency is decreased. Alk. hydrolysis is more destructive than acid hydrolysis. The lowered value may be due to such factors as loss of certain important amino acids or unknown building

stones, the toxic effects of certain free amino acids or some of their products of metabolism, or the possible importance of certain peptides. In the concns. used cystine, histidine, glucosamine, and cystine in the presence of tyrosine retarded and tyrosine, tryptophan, lysine, and arginine slightly stimulated yeast growth. Proline was without effect. In the presence of hydrolyzed edestin, however, cystine, tyrosine, or both together, stimulated growth; tryptophan, proline, lysine, and arginine acted similarly but only to a slight extent. Slight changes, increase or decrease, in concn. may easily cause a retardation but the general tendency is toward a retardation in growth with increased concn. of the amino acid. In those cases where the most marked growth stimulation was observed the amt. of additional yeast N found was considerably more than the N introduced as amino acid; this was the case especially with cystine and tyrosine. The beneficial effect cannot thus be due simply to its being a source of N.

A. P. LOTHROP

GUILLIERD, ALEXANDRE: *The Yeasts*. New York: Book Dept. of "Sugar," 153 Waverly Pl. \$6.00. Reviewed in *Sugar* 24, 338(1922).

#### D—BOTANY

B. M. DUGGAR

A quantitative study of the effect of anions on the permeability of plant cells. II. O. L. RABER. *Am. J. Botany* 8, 366-8(1921); cf. *C. A.* 14, 2360.—The present study extends the list of anions previously reported and includes both org. and inorg. compds. Na salts offer fewest difficulties and were used in each case. The salts used were the chlorate, sulfite, dichromate, molybdate, arsenate, ferrocyanide, formate, lactate, butyrate, propionate and salicylate. The results indicate that the effect on permeability depends upon the valence of the anion regardless of whether the salts are org. or inorg.

M. S. ANDERSON

The effect upon permeability of multivalent cations in combination with multivalent anions. O. L. RABER. *Am. J. Botany* 8, 382-5(1921).—Permeability studies made with salts of Mg and Al show that bivalent and trivalent cations in combination with univalent anions produce an increase in elec. resistance of *Laminaria*, but when combined with bivalent or trivalent anions the increase is less and may be entirely lacking.

M. S. ANDERSON

The effect upon permeability of (I) the same substance as cation and anion, and (II) changing the valency of the same ion. O. L. RABER. *Am. J. Botany* 8, 464-70(1921).—Cr has a different initial effect upon the permeability of *Laminaria*, depending upon whether it occurs in the anion or cation of a salt. If it is in the anion, the first effect is a decrease in the resistance, and if in the cation, an increase. In the case of Fe with a variable valency  $\text{FeCl}_3$  causes a greater increase in resistance than  $\text{FeCl}_2$ , independent of the H-ion concn.

M. S. ANDERSON

Vitamin requirements of *Drosophila*. I. Vitamins B and C. A. W. BACOT AND ARTHUR HARDEN. *Biochem. J.* 16, 148-52(1922).—The development of *Drosophila* requires the presence of vitamin B but not of vitamin C.

B. H.

Biochemistry of plant diseases. III. Effect of Sclerotinia cinerea on plums. J. J. WILLAMAN AND W. M. SANDSTROM. *Botan. Gaz.* 73, 287-307(1922).—The lab. inoculations recorded corroborate the field observations on plum varieties as to the relative resistance to the brown rot fungus.

BENJAMIN HARROW

Influence of wheat seedlings upon the hydrogen-ion concentration of nutrient solutions. L. H. JONES AND J. W. SHIVE. *Botan. Gaz.* 73, 391-400(1922).—An initial  $p_H$  value close to the neutral point is shown by Crone's and Sachs' soils. The others range between  $p_H$  4.0 and 4.8. The  $p_H$  value of Crone's and Sachs' soils remained

practically unaltered during the entire period of contact with the plant roots. Of the solns. with initial  $p_H$  values below 5.0, Shive's soln.  $R_4C_4$  exhibited the highest resistance to change (during a period of 52 hours throughout which the solns. remained in contact with the plant roots), while Tottingham's soln.  $T_2R_4C_4$  showed only slightly lower buffer properties. The solns. of Schreiner and Skinner, and of Hartwell, Wheeler, and Pember possess relatively low buffer actions. The compn. of these solns., as well as references to the original literature, is given.

BENJAMIN HARROW

**Occurrence of thiocyanic acid in plants.** S. DEZANI. *Stas. sper. agrar. ital.* 53, 438-60(1920).—HCNS was absent from exts. of the bulbs of *Allium cepa*, the seeds of *Phaseolus vulgaris* and *Pisum sativum*, wheat flour, carrots, apples, chicory, endive (leaves), spinach. Positive reactions were, however, obtained in exts. of the roots of *Brassica rapa*, *Cochlearia armoracia* and *Raphanus sativus*, in the fresh leaves of *Raphanus raphanistrum*, *Thlaspi bursa pastoris*, *Colepina corvini*, *Sisymbrium alliaria*, *Sisymbrium officinale*, *Nasturtium officinale*, *Bunias erucago*, *Eruca sativa*, *Sinapis alba*, *S. nigra*, and *S. arvensis*. Positive reactions in the case of hay are probably due to the presence of cruciferous plants. The HCNS where found is probably present as such and is not a decompn. product of allylthiocarbimide.

J. C. S.

**An abnormal permeability (of epidermal cells) for urea solutions.** K. HÖFLER AND A. STYRÖLKER. *Ber. botan. Ges.* 39, 157-64(1921); cf. Höfler (*C. A.* 12, 2345).—The authors have studied the permeability of the epidermal cells of *Gentiana Sturmiiana*, Kern., for urea by means of observations on the vol. changes of protoplasts in sections immersed in urea solns. The values obtained are many times greater than the corresponding values for other plants. The exceptional behavior of *Gentiana* is also shown in the ratio permeability for urea to permeability for  $KNO_3$ . The epidermal cells show a much higher permeability for urea than the ground tissue, a fact which has also been observed in the case of certain other plants.

J. C. S.

**Biogenesis of oil of peppermint.** R. E. KREMER. *J. Biol. Chem.* 50, 31-4(1922).—There is great similarity in the reactions by which the menthol group in peppermint (*Mentha piperita*, var. *officinalis*) and the carvone group in spearmint (*Mentha spicata*, Hudson) are elaborated. The two groups may have the common precursor, citral from which they are derived by a reaction involving the addition of 2 atoms of H—the difference being only in the point of reduction, in one case to an aldehyde group and in the other to carbon double bond. It is suggested that it may be a Mendelian "factor" which governs the conditions affecting the reduction of the citral. The striking parallelism in the relations of analogous compds. in the two oils suggests a common mechanism of formation. A great opportunity exists in the study of these common plants for the elucidation of phenomena which may be hereditary in character.

A. P. LOTHROP

**A saponin from Agave lechuguilla Torrey.** C. O. JOHNS, L. F. CHERNOFF AND ARNO VIEHOEVER. *J. Biol. Chem.* 52, 335-47(1922).—*Agave lechuguilla* Torrey grows abundantly on the limestone highlands of western Texas and in parts of Mexico and New Mexico. A new saponin has been isolated from its root-stock with attached roots and short overground axis and the base of the leaves. Its empirical formula has been detd. to be  $C_{57}H_{104}O_{12}$ . On hydrolysis it yields glucose and a prosapogenin. This prosapogenin yields galactose and an end-sapogenin to which the formula  $C_{43}H_{84}O_8$  has been assigned, the latter substance being identical with a sapogenin obtained from a saponin from *Yucca filamentosa*. The saponin occurs in the cell sap and may be located in the air-dried plant in the fibrovascular bundles or veins of the roots, rootstock, axis, and leaves. The rootstock and roots, apparently contg. the largest amts., yielded in an air-dried state about 9% of crude saponin. A 0.01% aq. soln. hemolyzed rabbit blood in about 1 hr. at 37°. The surface tension at 37° in Locke's soln. was 56.75 dynes per cm. The saponin is more toxic for fish than that from common soapbark,



*Quillaja saponaria*, or from the Cal. soap-plant, *Chlorogalum pomeridianum*. The saponin is sol. in  $H_2O$ , alc., and phenol. It is not pptd. by  $(AcO)_2Pb$ ,  $Pb$  subacetate, or  $Ba(OH)_2$ , and does not form an insol. compd. with cholesterol. A. P. LOTTEROP

The chemical constituents of green plants. XV. The occurrence of lactic acid in the leaves of the raspberry (*Rubus idaeus*). H. FRANZEN AND E. STERN. *Z. physiol. Chem.* 115, 270-83 (1921); cf. *C. A.* 16, 1795.—Considerable quantities of lactic acid were found. A critical review of the reported finding of lactic acid in other plants leads to the conclusion that it has been identified with certainty only in *Papaver somniferum*, *Ricinus communis*, *Agave sisalana* and *Tamarindus indica*. R. I. S.

The part played by the different constituents of the wood of the cade tree in the formation of oil of cade. R. HUERRE. *J. pharm. chim.* 25, 165-73, 214-21 (1922); cf. *C. A.* 15, 3366; 16, 312, 788.—Oil of cade results from the action of heat on 2 groups of substances contained in the wood: The light oil is yielded by  $H_2O$ -sol. elements, an essential oil, a resin sol. in petroleum ether and in  $Et_2O$  (A), another sol. in  $Et_2O$  alone (B). Tars heavier than  $H_2O$  are yielded by a resin sol. in  $AcOEt$ , and by the woody substance itself. The oils from resins A and B are, like the essential oil, solvents for the heavy tars. Woods poor in essence yield but little oil of cade. If they are also poor in resins A and B, they will yield but traces of the oil, or none at all. In these cases, the heavy tars are solvents for the small amts. of light oils distg. S. W.

Oregon balsam (HOLMES) 17.

DIXON, H. H.: *Practical Plant Biology*. London: Longmans, Green & Co. 291 pp. 6s.

## E—NUTRITION

PHILIP B. HAWK

### NORMAL

Sterilization of the intestines during fasting. S. DOMBROWSKI AND S. KOZLOWSKI. *Bull. soc. chim. biol.* 4, 71-9 (1922).—Study of a 13-day fast in a young adult gave the following results: Etheral sulfate and indican increased slightly in urine in the first day, then fell to less than 1/10 the original values. Bilirubin and unchanged cholesterol appeared in the feces from the 4th day. Bacterial action decreased sensibly on the second day, and reached its min. on the fourth. A. T. CAMERON

Effect of thyroid feeding on rats on a vitamin-deficient diet. A. T. CAMERON AND A. MOORE. *Trans. Roy. Soc. Canada* 15, Sect. V, 29-36 (1921); cf. *C. A.* 16, 1798.—The effect on total growth is additive. No definite conclusions can be drawn from the results for hypertrophy of body organs. A. T. CAMERON

The function of the lymphocyte and of lymphoid tissue in nutrition, with special reference to the vitamin problem. W. CRAMER, A. H. DREW AND J. C. MOTTRAM. *Lancet* 1921, ii, 1202-8.—Absence of the  $H_2O$ -sol. B vitamin from the diets of mice and rats leads to an atrophy of the lymphoid tissue throughout the body and to a lymphopenia in the circulating blood. The polymorphonuclear leucocytes are not affected. Absence of the fat-sol. A vitamin does not lead to an atrophy of the lymphoid tissue and there is no lymphopenia. Absence of the  $H_2O$ -sol. B vitamin leads to characteristic nutritional disturbances such as loss of wt., emaciation, subnormal temp. which may be designated by the term "marasmus." No such marasmus results from withholding the fat-sol. A vitamin. This condition can also be produced by other processes which destroy lymphocytes such as X-ray exposure, indicating that the lymphocytes play an important role in nutrition. The conception that vitamins—and the B vitamin in particular—are necessary for the life of every individual cell is criticized. The vitamin is necessary for the maintenance of life of a highly differentiated animal, not because it

presence is necessary for the life of all the cells of such an animal, but because its presence is necessary for the normal functioning of lymphoid tissue. E. B. FINK

The effect of B vitamin on the appetite. SAMSON WRIGHT. *Lancet* 1921, ii, 1208-9. —Vitamin B acts by facilitating the efficient carrying out of the functions of the intestinal canal. The main effects produced by the absence of the vitamin, *i. e.*, diminished food consumption, loss of wt., and ultimate death, are due to intestinal stasis and the absorption of toxic bodies which results therefrom. E. B. FINK

Further investigations on the nitrogen minimum. K. THOMAS AND H. STRACZEWSKI. *Arch. Anal. Physiol., Physiol. Abt.* 1919, 249-62; *Physiol. Abstracts* 6, 138-9. —An attempt was made to learn the stages of protein breakdown on a minimal protein intake with abundant carbohydrate; the amino acid chosen for tracing was cystine. If bromobenzene is given by the mouth or subcutaneously, any intermediary free cystine is excreted as bromophenylmercapturic acid when the dogs are given mixed diet; not so with protein starvation, in which no trace of the cystine deriv. is excreted. Conclusion: Under these conditions protein is not broken down in the ordinary autolytic fashion. H. G.

Coffee and vitamins. P. DI MATTEI. *Policlinico, sez. prat.* 27, 1011-3 (1920); *Physiol. Abstracts* 6, 140. —Roasted coffee contains vitamin capable of curing "polished rice" neuritis. Excessive feeding on vitamin produces no characteristic effect. H. G.

Calculations in basal metabolism determinations. J. H. SMITH AND M. C. SMITH. *Boston Med. Surg. J.* 186, 641-2 (1922). —A chart of graphs is presented by the use of which the calcs. in basal metabolism detns. are simplified. JULIAN H. LEWIS

The utilization of calcium and phosphorus of vegetables by man. N. R. BLATHERWICK AND M. LOUISA LONG. *J. Biol. Chem.* 52, 125-31 (1922). —Ca and P derived from vegetables are capable of meeting the maintenance requirements of man. The vegetables used were cabbage, celery, squash, spinach, lettuce and asparagus. The P metabolism in diabetics is not, therefore, affected by lowering the protein intake if adequate amts. of vegetables low in carbohydrate are allowed. A. P. LOTHROP

The nutritional adequacy of the proteins of the Chinese and Georgia velvet beans with reference to amino-acid composition. D. B. JONES, A. J. FINKS AND H. C. WATERMAN. *J. Biol. Chem.* 52, 209-10 (1922). —The proteins of raw Georgia velvet beans are not inadequate on account of amino-acid deficiency and cystine is not a growth-limiting factor as claimed by Sure (*C. A.* 16, 1108). Finks and Johns (*C. A.* 15, 3512) have shown in feeding expts. that growth at the normal rate occurs without the addition of any supplementary amino acid or protein whatever, provided an indigestibility is removed by heating the meal with distd. H<sub>2</sub>O for a short time or by feeding coagulated preps. of the proteins. Sure makes no reference to these expts. of Finks and Johns and conveys the impression that the statement of Waterman and Jones that there is no amino-acid deficiency in these proteins was based solely on chem. analyses and digestion expts. *in vitro*. A. P. LOTHROP

The antiscorbutic vitamin. I. A study of its solubility from desiccated orange juice. E. B. HART, H. STEENBOCK AND S. LEFKOVSKY. *J. Biol. Chem.* 52, 241-50 (1922). —The antiscorbutic vitamin of desiccated orange juice is sol. in 80, 95, and 100% EtOH. It is also sol. in MeOH. The investigations of others show that it is also sol. in H<sub>2</sub>O, but these expts. do not exclude the influence on soly. of the salts inherent in the material extd. This vitamin is insol. in BuOH as well as in C<sub>6</sub>H<sub>6</sub>, petrol-ether, Me<sub>2</sub>CO, Et<sub>2</sub>O, CHCl<sub>3</sub>, and AcOEt. The behavior of this vitamin toward org. solvents and H<sub>2</sub>O indicates that it is not of fat or lipid character. The solvents in which the vitamin was insol. did not destroy the vitamin as the residue after treatment with the solvent had antiscorbutic properties in each case. A. P. LOTHROP

**Digestibility of raw rice, arrowroot, canna, cassava, taro, tree-fern, and potato starches.** C. F. LANGWORTHY AND H. J. DEUEL, JR. *J. Biol. Chem.* **32**, 351-61 (1922).—Each of the starches under consideration was eaten as the principal constituent of a frozen pudding, resembling ice cream in texture and flavor, of which the starch made up about 20%. Raw corn, wheat, cassava, rice and taro root starches were completely digested when eaten in amts. as large as 250 g. per day. Raw tree-fern and true arrowroot (*Maranta arundinacea*) starches were nearly completely digested but some starch was present in the feces (estd. digestibility 93.4 and 95.7% resp.). Raw com. arrowroot (*Zamia floridana*) and potato starches showed considerably less complete digestion, as large amts. appeared in the feces (estd. digestibility 82.5 and 78.2%, resp.). Raw canna starch was even less digestible, its coeff. being only about 50%. There seemed to be a direct relationship between the size of the starch granules and its digestibility but it was not possible to det. whether this relationship was accidental or not. One might readily suppose that the larger starch granule contained a thicker cellulose covering and consequently one more impervious to the digestive ferments than the smaller granule. The factor of surface area might also come into consideration since the larger the granule, the proportionately smaller area for being attacked. In the case of the larger granulated starches there appeared to be a much larger variation between the ability of different subjects to digest the raw starch than could be accounted for on the basis of expl. error. The large number of digestion expts. previously conducted have, with the possible exception of some expts. on bran, demonstrated no greater variation in the ability of the digestive organs of different individuals than might be attributed to expl. error. There are also indications that smaller quantities of a given starch might be more completely digested but additional expts are necessary to prove this conclusively.

A. P. LOTEROP

**The mineral metabolism of the milch cow.** E. B. FORBES, J. A. SCHULZ, C. H. HUNT, A. R. WINTER AND R. E. REMLER. *J. Biol. Chem.* **52**, 281-315 (1922).—The Ca metabolism of the milch cow, while fed on winter feeds, is characterized by rapid loss from the body during the early part of the period of lactation, changing to retention late in the period of lactation, by continued retention during the dry period, with most rapid storage at the end of the period of gestation. The principal factors detg. the loss of Ca during the early part of the period of lactation are the impulse to secrete milk, as accentuated by selective breeding and a limited ability to assimilate Ca. There were 49 negative Ca balances during liberal milk production, without one exception. The largest milk production with which there was Ca retention was 9.98 lbs. It is considered likely that Ca retention can occur during more extensive milk production. The dry cow, on dry feeds, can store Ca at a rate at least equal to that at which the fresh cow, on dry feeds, loses Ca. The loss of Ca from the body appears to be a prominent factor in the nutritive depletion and the functional rearrangement of the overtaxed milch cow. The ability of the cow to assimilate Ca is much more definitely limited than her ability to assimilate N. The Ca of the bones is more readily available for purposes of milk elaboration than the Ca of the ration and of mineral supplements. It is not clear that supplemental Ca is utilized, either during lactation or during the dry period. There was no evidence of a tonic effect of Fowler's soln. in relation to Ca or other mineral retention. A marked but not complete interdependence of Ca and P in metabolism was manifest. P may be stored during liberal milk production; Ca seems never to be stored under these conditions, at least on winter rations. A positive N balance probably favors Ca retention to a slight extent but the measure of independence existing in the metabolism of N and the mineral elements is prominent. There is a considerable but not complete interdependence of N and S in metabolism. The av. apparent digestibility of the protein of the expl. rations was 66.23%; of the N-free ext., 78.64%.

of the  $\text{Et}_2\text{O}$  ext., 65.02%; and of the crude fiber, 36.33%. The proportionate elimination of minerals by urine and feces bears no definite relation to mineral balances. Many negative mineral balances were detd. which could not signify insufficient intake. The concept of milk including the colostrum suggests that its laxative character is due to physiol. "salt action." The milk of the cow was found not to contain As during the administration of 0.287 g. of the element per day in the form of Fowler's soln. The milk toward the end of the period of lactation was found to differ from that of the middle of this period by being richer in N and in all of the minerals except K, which was distinctly low. Na and Cl were in greatest excess. Ca was eliminated in the urine in the smallest amt. by the freshest cows. Cl excretion in the urine was low in the milking cows and high in the dry cows. A high proportion of grain in the ration produced a marked increase in the urinary outgo of P, apparently as an expression of acidosis. The physiol. antagonism of Na and K, and of Ca and Mg, is not discernible in the metabolism of practical rations and the considerable variety of mineral supplements used. The results suggest the desirability of building up extensive mineral reserves in growing heifers by liberal allowance of feeds rich in mineral nutrients, and also the importance of a dry, resting period of adequate length to permit the restoration of all previous nutrient overdrafts, with liberal feeding during this period.

A. P. LOTHROP

**Nutritive value of fats and lipoids.** I. KATSUMI TAKAHASHI. *J. Chem. Soc. (Japan)* 43, 201-42(1922).—Nutritive values of different lipins are given. Cholesterol, lecithin, cephalin and protagon were prepd. from horse brain and purified by the usual methods. Pure fatty acids were prepd. either by T. or by purification of com. products and their triglycerides were synthesized. Triacetin, tributyrin, trivalerin, tricaproin, tricaprylin, tricaprin, trilaurin, trimyristin, tripalmitin, tristearin, triarachin, tricerotin, triolein, and trilinolein were used.  $\text{H}_2\text{O}$ -sol. B was tested with pigeons and fat-sol. A with albino rats. Pigeons were fed with a diet lacking  $\text{H}_2\text{O}$ -sol. B, until the deficiency symptom was apparent, and then one group of the birds was fed with different lipins; into the others lipins were injected intraperitoneally. Cholesterol, lecithin, cephalin and protagon do not contain  $\text{H}_2\text{O}$ -sol. B, although the last gives temporary relief in both groups of animals. These lipins also do not contain fat-sol. A (cephalin showed temporary improvement). These lipins not only do not contain these vitamins but also show detrimental effect upon the animals (more so with males than with females). This effect is greatest with cholesterol; during a very early stage of the growth it lowers resistance to diseases. These lipins may have an intimate relationship with sexual activity of the animals. None of the triglycerides used had an action identical with that of fat-sol. A. Nutritive values of these fats in absence of fat-sol. A depends upon the nature of the fatty acids. It is not a function of m.ps. of the fats, but is closely related to their mol. wts. Among the glycerides of non-volatile fatty acids, the greater the wt. of the fat, the less its value, while in glycerides of volatile fatty acids, the reverse is the case. In general, the smaller the sapon. no., the less satisfactory is the fat. Physiol. action of fat-sol. A is discussed in detail. This vitamine has no direct action upon the growth of animals, but is an accessory factor important to fat metabolism which is directly responsible for growth. Nutritive values of the fats are dependent not only upon the content of fat-sol. A, but also upon the nature of the fats. Some lipins, like cholesterol, have an anti-growth effect. Supplementary expts. are cited to show that the presence of digestible carbohydrate is not absolutely necessary for nutrition. Fifteen charts and several tables are given to show the results of the nutrition expts.

S. T.

#### ABNORMAL

**Rickets:** a theory of the metabolic disturbances and of its association with tetany. D. N. PATON. *Brit. Med. J.* 1922, I, 379-81; cf. C. A. 16, 2168.—An error in the

metabolism of lecithin, probably in the liver, may be a causal factor in the failure of bone formation in rickets; this may in some cases be accompanied by increased conversion of choline into guanidine compds., explaining the association of tetany with rickets.

A. T. CAMERON

Metabolism of children undergoing open-air treatment, heliotherapy, and balneotherapy. L. HILL, J. A. CAMPBELL AND H. GAUVAIN. *Brit. Med. J.* 1922, I, 301-3. —Measurements on children with surgical tuberculosis, made at Alton and Hayling Is. by the Douglas-Haldane method, gave admission figures 30% above standard and after 3 months treatment 50% above. They were made at comparable times after meals. The hospital diet is considered to produce a 10% increase. The rise after treatment is attributed to open-air exposure. Measurement in a room at 70° F. decreased the figures.

A. T. CAMERON

Resting metabolism of children and adults in Switzerland. L. HILL, J. A. CAMPBELL AND B. HUDSON. *Brit. Med. J.* 1922, I, 385-6. —High results were obtained (59 to 225% above basal figures for children suffering mainly from surgical tuberculosis; 38 to 79% for normal and psychical adults). The figures were obtained 2-3 hrs. after a Continental breakfast, considered to increase basal metabolism only 2%. The chief cause of the high results is considered to be exposure to the higher atm. cooling powers.

A. T. CAMERON

Digestion of fat and the diagnosis of pancreatic insufficiency. M. LABBÉ AND H. FREISE. *Ann. méd.* 7, 424-35(1920); *Physiol. Abstracts* 6, 137. —A detailed method is given for the estn. of the degree of utilization of total fat, neutral fat, fatty acids, soaps, and unsaponifiable fat of a diet. Although the utilization was less perfect in conditions of pancreatic insufficiency, the very considerable reduction in the degree of splitting of neutral fat previously described was observed. But in the absence of the pancreatic secretion this splitting was probably only at all complete in the lower portions of the intestine.

H. G.

Nitrogen and fat metabolism of an infant with a congenital obstruction of the bile duct. E. FREISE. *Monatsschr. Kinderheilk.* 18, 515-20(1920); *Physiol. Abstracts* 6, 198. —In a 7 months old infant with congenital obstruction of the bile duct the utilization of the fat and N of the milk diet was found to be much reduced.

H. G.

A study of the metabolism and respiratory exchange in poultry during vitamin starvation and polyneuritis. R. J. ANDERSON AND W. L. KULP. *J. Biol. Chem.* 52, 69-89(1922). —The first apparent effect on poultry of a diet of polished rice is loss of appetite and food consumption decreases until finally the food is refused entirely. Loss in wt. is gradual but continuous and a similar decline in heat production occurs. The fall in the intensity of the metabolism is coincident with the decrease in food consumption but it depends upon some factors outside of mere voluntary consumption of food, because if the animals are forcibly fed, the utilization of such food is much delayed. The continued lack in the diet of vitamin B evidently causes a serious impairment of the digestive functions, which, during polyneuritis, results in a practical cessation of digestion and assimilation. In vitamin starvation there is no noticeable change in the respiratory quotient. During the first 3 or 4 hrs. after feeding rice, quotients approaching or exceeding unity were observed for a short time before polyneuritis developed. About 18 hrs. after feeding rice the av. respiratory quotients ranged from 0.73 to 0.82. The most striking effect in vitamin starvation is the inability of the animals to utilize a normal quantity of food and the consequent decline in heat production. In some cases the heat production fell 40-50% below the normal basal metabolism. The metabolism sinks to a very low point when polyneuritis has progressed so far that symptoms of paralysis appear. The respiratory quotient seldom rose above 0.75 during this stage of polyneuritis, although the crop contained much undigested rice, indicating an almost

complete inability at that time to utilize this food. Undigested rice was found in the crop and gizzard more than a week after the last feeding. The heat production falls to 50% or more below the normal basal metabolism. After the animal recovers from polyneuritis the metabolism and the heat production rise rapidly but the appetite remains poor and the gain in wt. is very slow.

A. P. LOYEROP

The "malt" disease among cattle considered as a deficiency disease. I. FOGNARU. *Compt. rend. soc. biol.* 86, 640-1 (1922).—In alc. distilleries cattle were fed on the residue left after the malt had been distd. The animals became very sick, and a large number of them died in cachexy. When guinea pigs were given this food they likewise developed symptoms of malnutrition and died, not however if fresh beets were added to the diet. Conclusion: The "malt residue" is devoid of vitamin which accounts for its defectiveness in nutrition.

S. M.

The etiology of rickets, early and late. H. S. HUTCHISON AND S. J. SHAH. *Quart. J. Med.* 15, 167-94 (1922).—The most important factor in the production of rickets is lack of fresh air, sunlight and exercise.

JOHN T. MEYERS

Experiments on carbohydrate metabolism and diabetes. V. The influence of glucose ingestion on diuresis and blood composition in non-diabetic and diabetic persons. J. W. SHERRILL AND H. J. JOHN. *J. Metabolic Res.* 1, 109-63 (1922).—Expts. on 19 persons, non-diabetic, mildly and severely diabetic. Upon the ingestion of 100 g. glucose or less it was found that a hyperglucemia accompanied by oliguria was produced in the normal and many diabetic subjects. The attendant fall in hemoglobin, red cell vol. and in the plasma Cl concn. point to a retention of H<sub>2</sub>O in the blood or tissues or both. The apparent diln. of the blood occurs during the period of hyperglucemia and oliguria in all typical cases, thus disproving the assumption that the oliguria is due to the concn. of the blood through the osmotic withdrawal of H<sub>2</sub>O by the intestine. Glucose does not normally act as a diuretic by osmotic influence on the kidney, oliguria being just as, or even more, pronounced in presence of marked glucosuria, hyperglucemia and hydremia. In a number of the more severe diabetic cases glucose did act as an active diuretic producing polyuria with or without hydremia. In none of the latter cases was the diabetes "total," for only part of the glucose was excreted or retained in the blood, the remainder being either utilized or stored. These varying degrees of sugar disposal appear to explain the nonuniform behavior of the diabetics towards diuresis.

W. A. PERLZWEIG

## F—PHYSIOLOGY

ANDREW HUNTER

Cholesterol content of blood in India. C. D. DE LANGEN. *Geneeskundig Tijdschr. Nederland. Indië* 62, 5 (1922).—L. finds that a comparatively high content of cholesterol in the blood of some Indian natives—0.16 to 0.18% as compared with 0.11% in normal humans—is chiefly due to food rich in cholesterol.

R. B.

The gaseous metabolism after fatiguing muscular work on a low-calorie diet. H. LIZDÖRER. *Arch. Hyg.* 88, 331-42 (1919).—The expts. were conducted on 2 men for 1 wk. The work was at first light but was changed to marching under severe conditions. The diet contained 1628 cal. and 60 g. protein. The principal changes in the respiratory exchanges were the results of deeper respirations and larger vols. of air inspired, due to heightened irritability of the respiration center. Tabulated results are appended.

JULIAN H. LEWIS

Further study on the micro-histochemical nature of the Nissl body and the "nucleoprotein-like granule." K. MARUI. *Mitt. allgem. Path. path. Anat.* 1, 413-9 (1922).—Further study of the micro-histochem. nature of the Nissl body showed

contrary to description of other authors, that it is sol. in HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> in a certain concn., if applied a sufficiently long time; the "nucleoprotein-like granule" (Marui) of neuroglia cells and granule cells gives the same reaction as the Nissl body in this respect. Parenchymatous cells of liver in rabbit, dog, cat, and also in man contain granules and granule groups, which give the same micro-histochem. reactions as the Nissl body and "nucleoprotein-like granule" of neuroglia cells; they were given the designation "nucleoprotein-like granule" of liver cells and "tigroid body" of liver cells, resp.

E. R. LONG.

Sedimentation velocity of the red blood corpuscles with reference to cholesterol and lecithin. H. KÜRZEN. *Arch. ges. Physiol. (Pflüger's)* 185, 248-61 (1920); *Physiol. Abstracts* 6, 128.—Cholesterol hastens, while lecithin retards sedimentation; hence the rate of sedimentation depends on the balance between the two substances in the plasma. The site of the effect is at the cell boundary.

H. G.

Biology of the placenta. S. PICCOLI. *Arch. Ostetr. Ginecol.* 8 (1920), reprint pp. 158; *Physiol. Abstracts* 6, 150.—The biological activities of the placenta are reviewed and discussed, but in particular the absorption of nitrogenous substances, carbohydrates, and mineral salts is dealt with. In the maternal and fetal blood there appears to be contained normally about the same amt. of amino N. If the amino N is artificially increased in the maternal blood, a similar increase occurs in the fetal blood, but a return to the normal equil. soon takes place, the amino acids being absorbed in part by the maternal, in part by the fetal tissues. The placenta of the dog contains normally about 0.03% of amino N, and during the passage of the amino acids it retains very small quantities, which are notably smaller than those absorbed by the muscles and liver of the fetus. Maternal amino acids pass probably unmodified through the placenta. A proteolytic or proteosynthetic function of the placenta to the advantage of the fetus appears neither necessary nor probable, the proteolytic enzymes of the placenta having very likely a limited action, simply connected with local metabolism. The same conclusions apply to the absorption of carbohydrates and mineral salts, and very likely also to that of fats. Conclusion: The essence of the exchanges between mother and fetus probably consists in a process of diffusion.

H. G.

The pressure of formation of lymph. G. JAPPELLI. *Arch. sci. biol.* 1, 193-224, (1920); *Physiol. Abstracts* 6, 135.—After intravascular injections of solns. of NaCl of different concns., the pressure under which the lymph flows from the thoracic duct shows the following changes: After the injection of hypertonic solns., the pressure, after a period of latency lasting 30 to 40 seconds, rapidly increases until it reaches a value which is about double that of the normal. After the injection of hypotonic solns. the pressure goes down to zero and the flow stops. After the injection of isotonic solns. the pressure increases, but the increase is small and there is no latency. This observation agrees with Starling's transudation theory. But the other two conclusions, and particularly the remarkable increase in the pressure following a period of latency after the injection of hypertonic solns. of NaCl, are not sufficiently explained by the transudation theory, and become only intelligible if one admits the participation of other factors such as changes in the osmotic pressure within and without the endothelial wall of the lymph vessels, as well as in the endothelial wall itself.

H. G.

Specific secretion of cells cultivated in vitro. C. CHAMPY. *Compt. rend. soc. biol.* 83, 842-3 (1920); *Physiol. Abstracts* 6, 116.—Cells of the prostate of the guinea pig cultivated in blood serum were found not to give the characteristic reaction with the contents of the seminal vesicles that is observed with the cells of the fresh gland. During cultivation *in vitro*, therefore, the cells lose their sp. secretory properties.

H. G.

Relation between actual reactions of the blood and urine. R. BÄHLMANN. *Dis.*

**Urethra.** 1920; *Physiol. Abstracts* 6, 145.—Expts. on the perfusion of the frog kidney with solns. of varying acidity. The urine was found in all cases to be more acid than the perfusion fluid, even when that was relatively strongly alk. Incidentally it should be mentioned that the perfusion was carried out through the aorta, and that ligation of the renal portal vein produced no appreciable effect on the urea and glucose concn. of the urine.

H. G.

**Creatine and creatinine.** T. TAKAHATA. *Milit. med. Fak. Univ., Kyushu* 5, 271-326(1920); *Physiol. Abstracts* 6, 142.—Numerous observations, from some of which T. concludes that creatine and creatinine play a role in the regulation of the body temp.

H. G.

**Extended resection of small intestines and contribution on the investigation of the metabolism of the cases concerned.** R. TOIDA. *Milit. med. Fak. Univ., Kyushu* 5, 373-90(1920); *Physiol. Abstracts* 6, 138.—A case of resection of 317 cm. (54%) of the small intestines did not show any disturbances of digestion. The motion was normal and regular—once or twice a day. The unabsorbed part of the proteins was about 17%, of fats 14%, and of carbohydrates 0.5%.

H. G.

**Physiology and pharmacology of kidney functions.** I. K. TAMURA AND M. MIWA. *Milit. med. Fak. Univ., Tokyo* 23, 317-48(1920); *Physiol. Abstracts* 6, 144.—The O consumption of the kidney does not vary greatly during normal secretion or during alteration in the velocity and vol. of the blood flowing through it, or even after injection of such diuretics as NaCl, Na<sub>2</sub>SO<sub>4</sub>, and caffeine. The authors conclude that whereas the kidney requires a good deal of energy for its upkeep, very little is necessary for the performance of secretion; they conceive of 2 types of permeability—phys. (passive) and physiological (active), the latter being comparable to the activity of true secreting glands, but differing from it in requiring much less energy.

H. G.

**Chemical composition of human gall bladder.** R. TOIDA. *Milit. med. Fak. Univ., Kyushu* 5, 327-35(1920); *Physiol. Abstracts* 6, 138.—Human bile obtained from the gall bladder by a puncture was analyzed. It was found to be richer in total solids than the liver bile. The bladder bile contained 40 times as much bile acids as the liver bile, and was 10 times richer in soaps, 9 times in fats, and 6 times in cholesterol and lecithin. Japanese appeared to have more soap and much less cholesterol, bile acids, and lecithin in their bile than Europeans. No difference was found between the bile of men and women.

H. G.

**New substances with hitherto unknown effect in human serum.** M. MANDELBAUM. *Munch. med. Woch.* 67, 1229-32(1920); *Physiol. Abstracts* 6, 156-7.—M. has demonstrated the existence in human serum of a substance which, when taken up by cells, has the power of destroying complement in fresh guinea pig serum. The substance is found in the globulin fraction of the serum, and arises when this is incubated at 37°. The substance is a thermolabile colloid, possibly the precursor of amboceptor.

H. G.

**The influence of exaggerated breathing on gas metabolism.** H. ILZHÖFER. *Arch. Hyg.* 83, 285-309(1919).—The effects of forced breathing were observed in 8 subjects for periods up to 1 hr. As the result of forced breathing there was a marked washing out of CO<sub>2</sub> from the body. At the end of the exp. the CO<sub>2</sub> tension was reduced 56% below normal. On return to normal breathing newly formed CO<sub>2</sub> is used to replenish the depleted stores of CO<sub>2</sub> in the body, but the amt. restored within a reasonable length of time is considerably less than that present normally. Estns. of blood reaction in 2 cases after forced breathing showed a small increase in alkalinity. The kidneys act as a protective mechanism by excreting large amts. of alkali.

JULIAN H. LEWIS

**The influence of carbon dioxide content of the air on breathing and gas exchange.** HERMANN ILZHÖFER. *Arch. Hyg.* 89, 223-36(1920).—A relatively small increase of



CO<sub>2</sub> in the air inhaled causes an increase in the vol. of respiration. The increase of the latter goes parallel with the increase of CO<sub>2</sub>. The vol. of respiration increases in the same way if the increased CO<sub>2</sub> is pure, made from combustion or from expired air, which indicates that CO<sub>2</sub> alone is responsible. The frequency and depth of respiration are not essentially increased by breathing air rich in CO<sub>2</sub>. The alveolar CO<sub>2</sub> tension is increased, the alveolar O tension only immaterially changed and the CO<sub>2</sub> excretion and O used are not markedly but unmistakably lowered. The lowering of the O used is dependent on and goes parallel with the CO<sub>2</sub> content of the air and is independent of the origin of the CO<sub>2</sub>. It is conditioned on the physical relations in the blood.

JULIAN H. LEWIS

**Creatine and creatinine metabolism. IV. The question of the occurrence of creatinine and creatine in blood.** JEANETTE A. BEHRE AND S. R. BENNETT. *J. Biol. Chem.* 52, 11-33(1922).—Creatinine does not occur in normal blood in detectable amts. and the color developed in protein-free blood filtrates by picric acid in the presence of alk. is due to some other chromogenic substance. When Na<sub>2</sub>CO<sub>3</sub> is added to a picric acid filtrate from blood there is a marked increase in color, which is far greater than can possibly be due to the presence of creatinine, since practically no detectable increase in color develops in solns. of pure creatinine in concns. such as have been assumed to be present in blood. When creatinine solns. contg. 2% NaOH are heated for an hr. the creatinine is completely destroyed but when filtrates from normal blood pptd. by H<sub>2</sub>WO<sub>4</sub> are heated with alkali under similar conditions, the blood "creatinine" remains practically unchanged. Creatinine added to such blood filtrates is completely destroyed while the original blood "creatinine" was practically unchanged. Furthermore true creatinine is removed from pure picric acid soln. or from blood filtrates quant. by kaolin up to amts. corresponding to about 3.5 mg. per 100 cc. of original blood, while the reactive-reacting substance is unaffected. By use of Lloyd's reagent it is possible to isolate minute amts. of creatinine from large vols. of soln. It has not been possible to isolate creatinine from blood filtrates by this method although added creatinine can be almost quant. recovered. It is not probable that true creatinine accumulates in the blood after impairment of the kidney function but more data are needed before a definite conclusion is drawn. *Creatine* is a normal constituent of blood and may occur in very appreciable amts. under certain conditions. It is converted into creatinine by heating the blood filtrates with HCl and when the procedures of heating with alkali and treatment with kaolin (mentioned above) are applied to blood filtrates of normal bloods after heating with acid, and compared with the "total creatinine" before and after such procedures, the color-producing substance resulting from the action of the acid is destroyed by alkali and removed by kaolin exactly as is pure creatinine. Creatine added to blood behaved in a similar manner. These results were obtained on beef and dog blood and although sufficient normal human blood was not available to warrant conclusions regarding it there is no reason for not believing that creatinine actually exists in human blood also. As to the occurrence of creatine in blood of patients with renal insufficiency the results have been so contradictory that it is likely that some of these bloods contain a large amt. of one or more interfering substances while in others the creatine figures are fairly exact. After ablation of the excretory function of the kidney of the dog by ligation of the ureters a marked accumulation of creatine in the blood occurs. This would seem to show that the creatine of the blood is essentially a waste product to be eliminated by the kidney and makes it highly probable that the kidney itself produces creatinine from creatine since creatine is not normally eliminated as such in the urine. The fact that ingested creatine does not appear in urine as creatine except in traces can be explained in several ways. These findings need not, of course, raise any question as to the value of the detn. of the chromogenic substance in blood for clinical or other

purposes. In all ordinary work the soln. or mixt. should be satd. with solid picric acid to give satisfactory results and even approx. satn. can only be assured by shaking the solns. in a shaking machine for 5-10 mins. prior to filtration. The use of the Folin-Wu pptn. with  $H_2WO_4$  is recommended followed by satn. of a portion of the filtrate with dry picric acid in a shaking machine for 5-10 min. After filtering the chromogenic substance is detd. by the original Folin method, using standard creatinine solns. in satd. picric acid.

A. P. LOTHROP

The partial pressure of oxygen in the blood during progressively induced anoxemia. CHAS. W. GREENE AND CARL H. GREENE. *J. Biol. Chem.* 52, 137-55(1922).—The % satn. of the arterial blood was directly detd. under conditions of progressively induced anoxemia. The proponents of the secretory theory have assumed that the capacity for O secretion exists but is called forth only during extreme O lack. The conditions of the expts. would seem to be adequate to call forth this mechanism. No evidence of such a mechanism was found. Nowhere was evidence obtained of an arterial O tension higher than that of the alveolar air. The current conception of a purely physical mechanism regulating the passage of O through the pulmonary epithelium is confirmed for all stages of anoxemia. When alveolar air was exposed to a simultaneous sample of arterial blood, O was absorbed by the blood and never the reverse. Section of the vagi was without effect on the degree of satn. of the arterial blood during progressive anoxemia. Exptl. animals must be maintained in a state of high circulatory and respiratory efficiency in order to secure the max. degree of satn. of the arterial blood. The lowering of the % satn. of the arterial blood in dogs breathing air progressively reduced in O tension closely parallels the dissociation curve detd. *in vitro* by Barcroft and Camis (*C. A.* 5, 518). The lowest O content in inspired air was 1.96% and the animal completely recovered on artificial respiration followed by natural breathing of atm. air. The blood was 94.1% satd. in 10 min. after respiration was reestablished.

A. P. LOTHROP

Catalytic effect of ammonia on the oxidation of butyric acid with hydrogen peroxide (WITZEMANN) 10.

## G—PATHOLOGY

H. GIBSON WELLS

The specificity of the local tuberculin allergy of man. JULIUS HOLLÓ AND RENÉE AMAR. *Beitr. Klin. Tuberk.* 47, 357-64(1921).—Tuberculin and diphtheria bouillon give about the same reaction degree and in about the same number of cases. The reaction to tuberculin being O = 20, I = 20, II = 9 and III = 16 cases, while the diphtheria bouillon results were O = 23, I = 17, II = 19, and III = 16 cases. In order to test the reaction in positive and negative tuberculin cases, 32 children from 1 to 10 years old were studied. Of 15 tuberculin-positive children there reacted to diphtheria bouillon O = 8, I = 7, II = 2 and III = 0 cases; while of 17 tuberculin-negative children there reacted O = 6, I = 7, II = 3 and III = 1 cases, indicating that tuberculosis infection did not greatly change the ratio of diphtheria bouillon reactions (See Sorgo, *Deut. med. Wochschr.* 1911, Nr. 22). The findings agree with those of Sorgo but the conclusions do not.

H. J. CORPER

Copper treatment of tuberculosis. The theory of copper action in the healthy and tuberculous. H. EGGERS. *Beitr. Klin. Tuberk.* 47, 373-422(1921).—In preliminary studies the systemic and local toxic action of Cu in the normal healthy body is considered. In summary 1%  $CuCl_2$  soln. given to rabbits subcutaneously in dose of 1 cc. per 400 g. wt. produces in a week, besides disturbances of the general well being of the animal, which is especially noticed as a loss in wt. and can produce death in the smaller animals, local tissue changes in the form of marked necroses. The local point

of attack is the vascular nervous system. The histologic changes in rabbits with general and circumscribed abdominal tuberculosis treated by the subcutaneous injection of 1%  $\text{CuCl}_2$  soln., and skin and circumscribed abdominal tuberculosis after local copper therapy were studied. A slight favorable influence upon the tuberculosis after subcutaneous Cu treatment in peritoneal, general and localized, infection with the bovine bacillus was observed when the treatment was given coincident with infection; a healing influence upon the disease as a whole was not discernable. Lecutyl salve applied locally to skin tuberculosis hastened healing superficially but aside from the thin new-formed epidermal layers (in spite of intensive treatment) the deeper cellular and caseous tubercles revealed well stained acid-fast rods. The influence of Cu upon tuberculous tissues is strictly limited to a local effect; a deep and distant action is not obtained. On account of the increased susceptibility of the vascular nervous system around tuberculous tissues the action of the Cu is greater in these than in normal tissues. The views of von Linden, the advocate of the Cu therapy, are not concurred in. An affinity of the Cu for tubercle bacilli does not exist, and an affinity for tuberculous tissues, a cumulation, could not be verified. The Cu treatment of tuberculosis cannot be considered to be a specific therapy.

H. J. CORPER

Oliguria following tuberculin injections. ARNOLD KIRCH. *Beitr. Klin. Tuberk.* 47, 429-32(1921).—Generally tuberculin injections result in an increased urinary excretion, which can be utilized for removing effusions, but in some cases a diminished urinary excretion was observed even in the absence of a fever reaction, especially in exudative chest and peritoneal inflammations. An overdosage of tuberculin is offered as explanation. The oliguric reaction may be used for differential diagnostic purposes in some cases, where the diagnosis lies between primary cardiac insufficiency with general stasis, and residual polyserositis tuberculosa with consecutive circulatory weakness and universal venous stasis. Other forms of tuberculosis besides the exudative serosa type were not studied for the presence of an oliguria following tuberculin administration.

H. J. CORPER

Alcoholic heterophilous sheep-blood antigens. HANS SCHMIDT. *Beitr. Klin. Tuberk.* 47, 433-63(1921).—Sachs and Guth (*Med. Klinik* 1920, No. 6) showed that heterophilous antigens were present in organs, by flocculation of alc. exts. dild. with NaCl soln. to which was added rabbit serum immune to sheep blood. These studies were elaborated upon; a flocculation occurred with alc. exts. of the organs of guinea pigs mixed with rabbit serum immune to sheep blood. The flocculation occurred with nearly all the alc. organ exts. The weakest was obtained with liver, because of the presence of bile constituents. No flocculation occurred with blood or body fat of the guinea pig. Certain alc. organ exts. from cats and dogs also gave flocculation, especially the lung exts., while organ exts. from man, rat and rabbit gave no flocculation. The animals could be grouped according to this reaction. The white mouse took an intermediate and variable position. With certain limits of experimentation the normal serums of man and the various animals gave no flocculation with the exts. of the animals of the guinea pig group. Altering the exptl. conditions, weaker ext. dilns. and larger serum amts. may change these relations, probably bringing into play the normal hemolysins for sheep blood. Rabbit immune serums for sheep blood only cause flocculation when contg. heterogenetic hemolysins. Guinea pig antisera for sheep blood, free from heterogenetic hemolysins, never cause flocculation with alc. exts. of heterophilous antigens from organs. There is only an indirect relationship between the property of flocculation of an immune serum and its hemolytic action, insofar as the latter, when bound to isogenetic antibodies, has nothing to do with the flocculation. On the other hand the flocculation goes along with a loss in the heterogenetic hemolysis and the reverse. The heterophilous sheep blood antigen is best extd. from fresh organs with alc.

abs.  $\text{CHCl}_3$ , acetone, ligroin, ether, and toluene give exts. which probably contain it, but on account of the presence of fat and lipid admixtures are unserviceable for the flocculation test. The same is true of alc. exts. from dried organs. Drop-by-drop diln. of the alc. exts. is recommended. Opalescence is not essential to good flocculation. An optimal diln. of the exts. exists but the exact amt. of antigen for the immune serum is of slight importance for flocculation. Flocculation diminishes with increase in NaCl concn.; but it can occur in distd.  $\text{H}_2\text{O}$  and isotonic glucose soln. The presence of NaCl is not absolutely essential. Small amts. of saponin inhibit flocculation. It goes hand in hand with an increase in the surface tension. Extn. with ether-alc. recovers the antigen from the flocculent ppt.

H. J. CORPER

So-called blood lipases in tuberculosis. III. A. FRISCH. *Beitr. Klin. Tuberk.* 48, 15-23(1921); cf. C. A. 16, 745.—Previously it was shown that fibrous and stationary cases of tuberculosis revealed a high, while caseous, exudative and cachectic processes revealed a low, lipase titer in the serum. Repeated serial exams. revealed that a clinical improvement went hand in hand with a rise in titer and *vice versa*. There was no parallelism between the L. T. (lipase titer) and the lymphocytes. In 46 cases no parallelism between the L. T. and the intracutaneous M. Tb. partigens (A. (albumin), F. (fatty acid) and N (neutral fat)) injection was found. There was, however, a parallelism in the intensity increase or decrease of the L. T. and the N allergy. Feeding of butter did not increase the L. T. Tabelon (isobutyl ester of oleic acid) given to cases of surgical tuberculosis did not increase the L. T. nor the N. allergy. In guinea pigs injections of M. Tb. N. did not increase the L. T. In cases of tuberculosis M. Tb. N. also had no definite effect upon the L. T. not attributable to other causes. H. J. C.

The present status of the partial antigen question and the immunization to fat. MAX LIEBKIND. *Beitr. Klin. Tuberk.* 48, 37-55(1921).—It was not possible to ext. the fats from tubercle bacilli by means of fat solvents ( $\text{CHCl}_3$ , ether, and abs. alc.) sufficiently to change their staining properties. Animals treated with these tubercle bacillus fats did not develop in their blood serum antibodies toward tubercle bacillus fat suitable for complement-fixation tests.

H. J. CORPER

The positive and negative phases of tuberculin sensitiveness. F. HAMBURGER AND K. PEYRER. *Beitr. Klin. Tuberk.* 48, 66-72(1921).—After a tuberculin injection producing fever a negative phase occurs lasting several days, and during this time a tuberculin injection of like size does not again produce fever; this is analogous to the negative phase in opsonic index.

H. J. CORPER

Seasonal variations in tuberculin hypersensitiveness. K. PEYRER. *Beitr. Klin. Tuberk.* 48, 137-44(1921).—A greater hypersensitiveness of the skin (Pirquet and Moro reactions) to tuberculin exists during the months of December to July in tuberculous children. Parallel with this higher sensitivity goes a greater morbidity of the ectoderm, with a spring peak in March and April, in that phlyctenulae and erythema nodosum, forms associated with tuberculosis, also reach a peak during these months, although other factors may be instrumental besides in these conditions. Among 57 meningitis cases studied no seasonal correlation could be established, but there seems to be a greater incidence of severe open cases of pulmonary tuberculosis in the spring.

H. J. C.

Bladder stones of silicic acid. A. SCHLICHT. *Pharm. Ztg.* 67, 316(1922).—These formations ordinarily consist of urates, oxalates, phosphates, cystin and  $\text{CaCO}_3$ . A sample emanating from a sheep consisted essentially of  $\text{SiO}_2$ , slightly contaminated with constituents of the urine.

W. O. F.

The effect of various substances on agglutinin production. WALTER PFENNIGER. *Centralbl. Bakteriol. Parasitenk. Abt. I, Orig.* 80, 200-13(1917); *Abstracts Bact.* 4, 159M.—The effect of intravenous injection of 0.1 N  $\text{Na}_2\text{SO}_4$ ,  $\text{SrCl}_2$ , NaBr, *m*-cresol, and Na propionate on agglutinin production was studied. These salts, particularly NaBr, were found markedly to increase agglutinin production.

H. G.

The action of colloidal metals on staphylo toxin and staphylo lysis. L. FÉVRE DE ARRIC. *Compt. rend. soc. biol.* 82, 1331(1919); *Abstracts Bact.* 4, 179.—Colloidal preps. of Ag, Au, Pt, Mn and Fe were tested. The potency of staphylo toxin was not altered by contact with the colloids of Ag, Au, or Pt. The colloidal Fe weakened the toxin, as did also to a greater degree the colloidal Mn. Colloidal Ag increased the lytic action of the staphylo lysis, largely because of its own hemolytic action. A mixt. of colloidal Pt and staphylo lysis is slightly less hemolytic than either component alone. Au and Fe caused little change, while the Mn markedly decreased the potency of the lysis.

H. G.

Sources of error in the Wassermann reaction due to the antigen. DURUP. *Compt. rend. soc. biol.* 83, 2(1920); *Abstracts Bact.* 4, 162.—The source of error in employing different antigens lies in the extreme sensitiveness of some antigens. An antigen prep. from syphilitic liver gives 15% more positive fixations than does an antigen prep. from heart.

H. G.

Experimental investigations on the persistence of stercobilin in spite of the obstruction of the hepatic duct. M. BRULÉ. *Compt. rend. soc. biol.* 83, 1390-1(1920); *Physiol. Abstracts* 6, 199.—In dogs with closed bile-duct no stercobilin could be found in the feces and no bilirubin or urobilin in the urine. But when jaundice had set in, these substances were excreted by the large intestine. (Cf. C. A. 16, 1443.)

H. G.

Acidosis. W. M. BAYLISS. *West London Med. J.* 25, 76-8(1920); *Physiol. Abstracts* 6, 135.—A general account of acidosis in relation to blood reaction and CO<sub>2</sub> content of blood and alveolar air. B.'s colorimetric method for the detn. of blood reaction is described.

H. G.

Respiration metabolism in exophthalmic goiter after X-ray treatment. NIKOLAUS ROTH. *Wiener Arch. inn. Med.* 3, 367-78(1922).—The respiratory gas interchange was studied in a small number of cases of exophthalmic goiter before and after treatment with X-rays. In acute cases the oxidation, which is usually greatly heightened in exophthalmic goiter, was markedly reduced and there was an improvement clinically. In a chronic case the respiratory metabolism was not affected by the X-rays. There was no improvement in clinical symptoms. A "forme fruste" in which there was no heightened oxidation showed no change in respiratory metabolism after X-ray treatment. It is probable that gas metabolism studies will afford a reliable means of regulating X-ray treatment in exophthalmic goiter, and even when the clinical symptoms show little change, the marked changes in metabolism indicate a profound change in the organism.

HARRIET F. HOLMES

Diabetic edema and acidosis. E. FÖLDES. *Wiener Arch. inn. Med.* 3, 469-98 (1922).—In diabetics spontaneous edema as well as exptl. edema induced by the administration of KHCO<sub>3</sub> only develops when there is a pronounced acidosis. The edema disappears and recurs with the compensation and reappearance of the acidosis. The av. vol. of the red blood cells is increased in acidosis and may be taken as a measure of the amt. of acidosis. Administration of a proper amt. of NaHCO<sub>3</sub> for several days, until the urine becomes alk. or less markedly acid, brings about a return to normal of the av. vol. of the red blood cells. A dose of NaHCO<sub>3</sub> sufficiently large to render the urine neutral or alk. compensates the acidosis and no edema results. If only so much NaHCO<sub>3</sub> is given that the urine still remains acid, the acidosis is uncompensated and edema results. If edema is already established, the administration of sufficient NaHCO<sub>3</sub> to render the urine alk. does not affect the edema.

HARRIET F. HOLMES

Experimental and clinical study of antitrypsin. ST. RUSZNYÁK, I. BARAT AND G. DANIEL. *Wiener Arch. inn. Med.* 3, 515-24(1922).—The blood serum probably contains several substances possessing antitryptic power which show different degrees

of thermostability. These antitrypsins are colloids and are not lipoids or combinations of proteins and fats. The trypsin-casin method of Fuld-Gross was tried in 500 cases of carcinoma or cases in which carcinoma was at one time suspected. No cases were included of exophthalmic goiter, advanced tuberculosis, pregnancy or diabetes, conditions in which the antitryptic action of the serum is altered. The antitryptic reaction did not prove to be specific for carcinomas. In 26% the reaction was negative in the case of carcinoma and in 31% positive in other conditions. Carcinomas accompanied by cachexia give a higher percentage of positive results, but this accompanies the cachexia rather than the carcinomas as it may occur in cachexia from other causes.

HARRIET F. HOLMES

The diagnostic value of the Gruber-Widal reaction. W. HERGT. *Deut. Arch. klin. Med.* 138, 18-27(1922).—The value of the Gruber-Widal reaction is not affected in most cases by the typhoid immunization given during the war. A positive reaction is seldom obtained 2 yrs. after such an immunization. A single test cannot differentiate a true typhoid infection from a persistent vaccine reaction. The points of differentiation are the height of the titer and the duration. Fluctuations in the titer, as is usually seen in typhoid infection, are missing in the vaccinated. An unsp. reaction is found usually in those diseases caused by organisms that have the same agglutino-genic properties or in diseases such as tuberculosis and influenza where there is a mixed infection with organisms that form agglutinins.

JULIAN H. LEWIS

The rest nitrogen of human blood and tissues in nephritis. IRENE BARAT AND GAZA HETENYI. *Deut. Arch. klin. Med.* 138, 154-64(1922).—The rest N of the tissues is normally higher than that of the blood. In diffuse hematogenous nephritis it is considerably increased. In acute nephritis as well as acute exacerbation of chronic nephritis the % of rest N in the blood exceeds that of the tissues. In the nephroses, amyloidosis and toxic nephritis caused by pathological increased protein destruction there is an increased rest N in the tissues. In outspoken chronic processes, especially those not primarily renal, but due to cardiac decompensation (benign nephrosclerosis) the % increase of rest N in the blood and tissues, if any, is of equal amt. A difference in the retention of N in the different organs could not be demonstrated.

JULIAN H. LEWIS

The function of fats in immune processes. II. Pneumococcus and streptococcus immunity. C. C. WARDEN. *J. Infectious Diseases* 24, 285-96(1919).—The theory is advanced, and expts. are cited to prove it, that the proteins of the pneumococcus produce an enduring and protective antiserum while the fats are responsible for the specificity of such a serum. A highly protective antiserum was also produced by injecting the cholesterol esters of the pneumococcus artificial antigen previously described (*J. Infectious Diseases* 23, 131(1918)). Rabbits immunized with the artificial streptococcus antigen produce a serum that will ppt. such an antigen and agglutinate streptococci. Rabbits immunized with a single fat, as Na oleate or Na palmitate, produce an antiserum which is sp. for the fat used. An antistreptococcus antigen will produce a reaction with Na oleate which agrees with the finding that oleic acid is a constituent of the streptococcus.

JULIAN H. LEWIS

Studies on the formol and Wassermann reactions. MANUEL ADMANGUÉ AND PEDRO GONZALES. *J. Infectious Diseases* 30, 443-4(1922).—Positive results were obtained with the formol reaction of Gaté and Papacostas (*Compt. rend. soc. biol.* 83, 1432(1920)) in 67% of cases of malignant tumors which gave negative Wassermann reactions. Serums of normal dogs, rabbits, guinea pigs, hogs, etc. were always negative, but often positive in pathologic conditions, especially in tenia, coccidia or other parasitic infestations. Conclusion: The formol reaction is not due to some sp. substance but to a relative increase of the usual constituents of normal serum, possibly globulins.

JULIAN H. LEWIS

Observations on the preparation of toxin-antitoxin mixture. P. G. HANSEN AND C. R. HIXSON. *J. Infectious Diseases* 30, 508-15(1922).—Extreme care in the prepn. of toxin-antitoxin mixts. is emphasized. This is necessary because of the fluctuation that may take place in a mixt. These are explained on the relative affinity which antitoxin has for prototoxoid, toxone and toxin fractions of a toxin.

JULIAN H. LEWIS

Chemical studies on intestinal intoxication. I. The presence and significance of histamine in an obstructed bowel. R. W. GERRARD. *J. Biol. Chem.* 32, 111-24 (1922).—The chem. and biol. action of closed-loop fluids may be accounted for by their content of free and combined histamine, although other toxins are surely present. The amt. of histamine found in the contents of isolated closed loops of both the large and small intestine varied in different samples but from 2-3 mg. of histamine dihydrochloride per 100 cc. of fluid was found to be a fair minimum av. A combined histamine of a peptide nature was found in 2 samples of loop fluid. Histamine may be present in sterile as well as loop mucosa so that this amine is not necessarily formed only through the agency of bacteria. Histidine was also present in loop fluid and mucosa in sufficient amt. to account for the presence of the histamine if the latter was entirely derived from it by decarboxylation. Since histamine is present in the normal gut, obstruction must involve an increased production of this amine, a change in its absorption or detoxication by the mucosa or all these factors; else no systemic symptoms could appear.

A. P. LOTHROP

Experimental studies in diabetes. III. The pathology of diabetes. I. Hydropic degenerations of islands of Langerhans after partial pancreatectomy. F. M. ALLEN. *J. Metabol. Res.* 1, 5-41(1922).—A microscopic study of stained sections of dog pancreases purports (a) to establish a positive microscopic diagnosis of active diabetes; (b) to complete proof of the island theory of diabetes; (c) to add to the evidence of identity of exptl. and clinical diabetes; (d) to explain permanent lowering of assimilation in diabetes consequent upon excessive diets; (e) to offer the only proved example of anatomic breakdown of cells due to over-stimulation of an internal secretory function. 2. Granule stains of the islands of Langerhans of the diabetic and non-diabetic pancreas. W. B. MARTIN. *Ibid* 45-51.—Sections of animal and human diabetic pancreases were studied by a neutral granule stain modified by the author. Differentiation of alpha and beta cells from each other and from surrounding tissue is sharp and clear cut. Evidence is adduced that the islands elaborate an internal secretion. Application of the stains to sections from animals confirmed earlier work of Homans (cf. *C. A.* 7, 1220) concerning hydropic degenerations of beta cells. No advantage is claimed for these granule stains in the study of diabetic pathology. The application of granule stains to human diabetic material did not furnish conclusive results. 3. Nervous influences in the etiology of diabetes. F. M. ALLEN. *Ibid* 53-73.—No influence of emotion upon the production of diabetes could be demonstrated. The Claude Bernard piqure, selected as the type of nervous lesion, seemed to be a genuine factor in producing diabetes in one predisposed dog. Complete sepn. of a pancreas remnant from its original nerve supply fails to give rise to diabetes or any demonstrable lowering of assimilation. The full endocrine potency may apparently be maintained without stimulation or regulation from any special nervous centers. Such isolation of the pancreas remnant also fails to affect either the occurrence or the rate of the hydropic degeneration in the islands, which runs parallel with the course of diabetes the same as when the nerve supply is left undisturbed. 4. The role of hyperglucemia in the production of hydropic degeneration of islands. *Ibid* 75-88.—Hyperglucemia induced in normal and partially pancreatectomized dogs did not produce vacuolation in the pancreatic islands. Vacuolation of islands occurred in some diabetic animals

with prolonged hyperglucemia without glucosuria. Phlorhizin dosage did not produce degeneration in the islands of normal animals, nor did it prevent degeneration of islands in diabetic animals, though blood sugar was kept continuously at or below normal level. The humoral stimulus to hydropic degeneration cannot be the excess of blood sugar but must be something more specific in connection with the diabetes. 5. The influence of circulatory alterations upon experimental diabetes. *Ibid* 89-95.—Alterations produced by operative methods in the venous and arterial circulation in the pancreas of dogs failed to alter the assimilative function or pancreatic structure in any way. 6. Pancreatitis in the etiology of experimental diabetes. *Ibid* 565-91. 7. Microscopic studies of the pancreas in clinical diabetes. *Ibid* 193-219. 8. The microscopic pathology of the pancreas in 570 unselected hospital cases. *Ibid* 221-249. 9. Literature and discussion. *Ibid* 251-279.—Review of diabetic pathology.

W. A. PERLZWEIG

Composition of the liver, especially its protein content, in disease. G. HOPFF-SEYLER. *Z. physiol. Chem.* 116, 67-95(1921).—Analyses are given showing the total wt., dry wt., total N, coagulable N, fat and ash of about 40 diseased livers. R. L. S.

Composition of a "rhinolith." L. DRÉBUCQUET. *J. pharm. chim.* 25, 306-6 (1922).—A bony concretion, 0.28 g., extd. from the nasal cavity of a soldier consisted of  $\text{Ca}_3(\text{PO}_4)_2$  79.5%,  $\text{CaCO}_3$  10.7%, insol. in HCl 9.65%. S. WALDBOTT

Experimental plethora in dogs and rabbits. E. B. KRUMBHAAR AND ALFRED CHANUTIN. *J. Exptl. Med.* 35, 847-71(1922).—Effects of repeated transfusions of blood on the blood-destroying and blood-forming app. of normal and splenectomized dogs and rabbits are described. Blood destruction and elimination, as measured by excretion, are greatly increased during the stage of plethora but still more so during "plethoric anemia." Despite intravenous introductions of large quantities of N in the form of whole blood, the total N, urea and  $\text{NH}_3$  in the urine and feces are not raised for some time after the onset of plethora. The normal organism is apparently able to store large quantities of blood or its decompn. products. Upon the onset of "plethoric anemia," there is an increase in urinary total N and urea excretion, which is lowered during the course of the anemia. Albuminuria is also found at this time. Blood pigment, chiefly in the form of hemosiderin, is deposited in enormous quantities in spleen, liver, lymph nodes, and bone marrow. Increased pigment deposition can still be found several months after transfusions have been stopped.

C. J. WAST

A new method of adding cresol to antitoxins and antisera. C. KRUMWIRDE AND E. J. BANZAF. *J. Infectious Diseases* 28, 367-73(1921).—A mixt. of equal parts of cresol and  $\text{Et}_2\text{O}$  is presented as a new preservative for antitoxins and sera. This mixt. is added in amts. necessary to give the required concn. of cresol. The addn. of this mixt. causes much less ppt. than does cresol alone. Subsequent pptn. is not necessarily limited by the  $\text{Et}_2\text{O}$ ; it is never greater than that in products contg. cresol alone. The mixt. of  $\text{Et}_2\text{O}$  and cresol is more strongly antiseptic than cresol alone. In therapeutic application, the  $\text{Et}_2\text{O}$  is not a disadvantage. In case of intravenously injected antitoxin, the indication that the  $\text{Et}_2\text{O}$  may under certain circumstances reduce the incidence of adverse reactions warrants further comparative work.  $\text{Et}_2\text{O}$  may be added to the antitoxin-toxin mixt. without disturbing the balance of the mixt.

JULIAN H. LEWIS

Phenol and cresol as preservatives in biologic products. PETER MASUCCI. *J. Infectious Diseases* 30, 379-87(1922).—A study of preservatives including cresol, ether-cresol, phenol and ether-phenol on serum and plasma brings out that: (1) cresol or ether-cresol changes the color of serum or plasma from a light yellow to a greenish yellow; (2) there is no marked difference in the amt. of ppt. formed on standing between sera treated with straight cresol or ether-cresol (Krumwiede and Banzaf, preceding abstr.).



(3) the ppt. formed in normal serum is mostly finely divided fibrin; (4) cresol hastens the formation of fibrin in plasma; (5) cresol lowers the surface tension of serum much more markedly than does phenol; (6) ether-cresol does not "burn" serum on acct. of a surface tension phenomenon; (7) cresol produces hemolysis rapidly with destruction of the hemoglobin while phenol produces only slight hemolysis with no effect on the hemoglobin under the conditions of the expt; (8) ether does not alter the course of hemolysis in itself or as ether-cresol or ether-phenol; (9) the lowering of surface tension in itself does not produce hemolysis, but substances which lower the surface tension are absorbed by the erythrocytes to a greater degree.

JULIAN H. LEWIS

#### H—PHARMACOLOGY

ALFRED N. RICHARDS

A new point of view in the use of diuretics. ED. CROUZEL. *Repert. pharm.* 34, 97-101(1922).—The salts of the alkali metals (except Na) and the alk. earth metals, certain glucosides, alkaloids, glandular secretions, etc., act directly upon the kidney or indirectly by nervous reflex. Water may act as a mechanical means of regulation or merely as an inert vehicle.

JAMES A. BRADLEY

A case of luminal poisoning. D. J. K. WETSELAAR. *Pharm. Weekblad* 59, 521-2 (1922).—A servant girl attempted suicide by taking 2.0 g. of luminal, but recovered after 2 days of coma. From the urine collected during this time (170 cc.) not a trace of luminal could be obtained. In similar cases of veronal poisoning large amts. of veronal have been found in the urine. The inference is that luminal, in contrast to veronal, is completely destroyed in the body.

A. W. DOX

Action of adrenaline on the albumin stored in the liver. H. STÜBEL. *Arch. ges. Physiol. (Pflüger's)* 185, 74-85(1920); *Physiol. Abstracts* 6, 147.—The granules, staining red with methyl-green-pyronine, which accumulate in the cytoplasm of liver cells of protein-fed rats disappear after subcutaneous injections of adrenaline.

H. G.

Significance of potassium on automatic impulses of the heart. R. KOLM AND R. P. PICK. *Arch. ges. Physiol. (Pflüger's)* 185, 235-47(1920); *Physiol. Abstracts* 6, 131.—The initiation of automatic impulses in the frog sinus and auricle is facilitated by KCl. CaCl<sub>2</sub> causes diastolic arrest of hearts perfused free of K, the systolic contraction being dependent on the simultaneous presence of K. KCl in doses which are non-toxic for the whole heart causes paralysis of the tertiary centers in the automatically beating ventricle; it can also inhibit the excitation of the automatic ventricle centers induced by Ca or Ba chlorides. The property possessed by K of resolving the contraction of hearts treated with Ca depends on the reinforcement of the impulses from sinus and auricle. The presence of K salts reduces the tendency of the ventricle to fibrillation. The K content of the blood and heart tissue is of importance in the maintenance of cardiac rhythm.

H. G.

The action of glycerol. III. J. SIMON. *Arch. Biol.* 1, 225-32(1920); *Physiol. Abstracts* 6, 131; cf. *C. A.* 15, 2673.—The addn. *in vitro* of glycerol to blood serum increases its d., viscosity, and cryoscopic index, but it lowers its sp. elec. cond. The same facts can be observed in the blood serum of animals in which glycerol was injected intravenously.

H. G.

The action of ions upon the frog heart. I. DE B. DALY AND A. J. CLARK. *J. Physiol.* 54, 367(1921).—Lack of K and Na and excess of Ca all increase systolic tone, and the duration of the elec. response. K has the most marked effect on the conduction of the elec. variation, while reduction of the Ca content or alteration of the  $p_H$  has little effect. K and Ca are antagonistic as regards the mech. response; with regard to the elec. response, they are either temporarily or only slightly antagonistic.

H. G.

**Abortion of syphilis by the use of the arsenobenzenes in the period of incubation.**

LOUIS FOURNIER AND L. GUENOT. *Presse méd.* 27, 554(1919); *Abstracts Bact.* 4, 99.—The arsenobenzenes, injected in 6 to 8 doses totaling 2 or 2.5 g., from a few days to 2 weeks after exposure to known syphilitics, have averted the disease in a number of cases, as detd. by absence of clinical symptoms, negative Wassermann tests, and normal pregnancies.

H. G.

**Mercury poisoning.** R. R. SAYERS. *Bur. Mines, Repts. Investigations No. 2354* (1922).—Hg poisoning occurs whenever Hg in finely divided form, as in fumes, oil suspension, or aq. soln., comes in contact with the skin, lung tissue or the digestive tract. The symptoms include stomatitis, salivation, tremors, with degenerative org. changes. Proper ventilation and personal cleanliness obviate most of the bad affects in those otherwise healthy. Hg appears to combine with the brain tissue and interfere with motor but not sensory nerves. The mucous membranes become inflamed and ulcerated. Anemia is almost always present, very marked if exposure covers a long period. Remedial measures are principally forced ventilation and personal cleanliness. Attention to hygiene including bathing, protection by clothing and masks, clean clothes, regular habits of elimination aided by Mg citrate are essential for health when exposure to Hg is continuous. Suggested rules are given in detail by which workers may avoid most if not all of the ill effects of Hg absorption.

H. C. HAMILTON

**The effect of digitalis in two cases of arrhythmia in diphtheria.** V. BIG AND CARL SCHWENSEN. *J. Infectious Diseases* 30, 308-12(1922).—In the acute stage of diphtheria there is often a fatal complex disturbance of the rhythm of the heart, probably the result of attacks of auricular flutter. In 2 such cases the administration of digitalis stopped the arrhythmia. The pulse tracings became normal with the exception of some extrasystoles.

JULIAN H. LEWIS

**The action of neoarsphenamine and neosalvarsan on the phagocytic activity of leucocytes.** RUTH TUNNICLIFF. *J. Infectious Diseases* 30, 545-9(1922).—In proper concns. neoarsphenamine and neosalvarsan may increase the phagocytic activity of leucocytes, both *in vitro* and *in vivo*. *In vivo* the stimulating effect is rapid and of short duration, occurring as a rule within 30 mins. after intravenous injection. Further study is necessary to det. what part, if any, this stimulus of the phagocytic activity of the leucocytes plays in the curative action of neoarsphenamine and allied products.

JULIAN H. LEWIS

**Chemical changes of the blood under the influence of drugs. I. Ether.** H. V. ATKINSON AND H. N. ETS. *J. Biol. Chem.* 52, 5-10(1922).—Blood samples were drawn after the dog had been under Et<sub>2</sub>O anesthesia for 2 hrs. and their compn. compared with that of samples taken before the animal was placed under Et<sub>2</sub>O and in many cases 24 hrs. afterward. On an av. the CO<sub>2</sub> capacity of the plasma decreased 36.9% but had returned to normal the next morning. The blood sugar increased 94% from 0.103 to 0.20% and was still 22.3% above normal after 24 hrs. The increase in creatinine amounted to 16.2% and was temporary. There was a drop in total fat of 11.7% followed by a rise of 26.7% in 24 hrs. There was practically no change in either lecithin or cholesterol. The normal *p<sub>H</sub>* was 7.38 and this was lowered 4.4% to 7.06 but returned to normal in the next 24 hrs. The cause of the rise in the sugar may be related to: (a) the increase in the H ion concn. which corresponds to a decrease in the *p<sub>H</sub>*; and (b) the decrease in the CO<sub>2</sub> capacity of the blood plasma.

A. P. LOTHROP

**Radium therapy and its dangers.** DES NOUETTES. *Chronique pharm.: Schweiz. Apoth. Ztg.* 60, 17-22(1922).—A review of the history of Ra and its therapy; an account of its dangers is based mainly on Mottram's work (*C. A.* 14, 3279).

S. W.

LAGUWEN, W. STORM VAN: *Pharmakologie für Zahnärzte* I. Leipzig: F. C. W. Vogel. 222 pp. Reviewed in *Kolloid-Z.* 30, 79(1922).

## I—ZOOLOGY

R. A. GORTNER

**Effect of light on growth in the mussel.** A. G. HUNTSMAN. *Trans. Roy. Soc. Canada* 15, Sect. V. 23-8(1921).—Where light was the only variable factor, the av. increase in growth of specimens of *Mytilus* kept in the dark for 43 days was 3.11 times as great as that of those exposed to light. A. T. CAMERON

**The unusual action of Mödinger potable water on salamander larvae.** K. HOFMANN. *Naturwissenschaften* 10, 46-7(1922).—Abnormally rapid development of salamander larvae in Mödinger H<sub>2</sub>O led to control expts. with the addn. of various compds. to distd. H<sub>2</sub>O. Larvae in CaCl<sub>2</sub>, MgSO<sub>4</sub>, MgCl<sub>2</sub> and K<sub>2</sub>HPO<sub>4</sub> solns. grew faster than normally. In K<sub>2</sub>CO<sub>3</sub> the larvae remained small and finally died. They were very susceptible to Li<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>S. Various physiological abnormalities appearing under these special conditions are described. C. C. DAVIS

**The chemistry of the ameba.** P. G. UNNA AND E. T. TIELEMANN. *Centralbl. Bakteriol. Parasitenk. Abt. I, Orig.* 80, 66-89(1917); *Abstracts Bact.* 4, 28.—Amebae from hay infusion were fixed upon a glass slide by means of the vapor of osmic acid. By treatment with various stains and preliminary treatment with various solvents, it is possible to det. something as to the chem. nature of the various parts of the ameba cell. These cell constituents are divided primarily into the basic proteins, the acid proteins, and the lipoids. Under the first heading, the basic proteins most difficultly sol. are stained with hematoxylin and are dissolved by a 1% trypsin soln. They are present in the inner nucleus, the outer nucleus, endoplasm, and ectoplasm. The more easily sol. basic proteins were stained also with hematoxylin. Those sol. in distd. water are present only in the endoplasm in the so-called "Wabeninhalt." Those sol. in 2% NaCl are present only in the "Wabenumgebung." The protamines are stained red with Giemsa stain and are not sol. in KOH or in pepsin. They are prominent only in the outer layer of the nucleus. Among the acid proteins the globulin is stained by polychrome methylene blue. It is sol. in 2% NaCl, and is present in the inner nucleus, and in the "Wabenumgebung" of the endoplasm and the ectoplasm. The albumoses, sol. in distd. water, are present in the "Wabeninhalt" of both the endoplasm and the ectoplasm. Lipoids such as fatty acids, glycerinated fats, cholesterol esters, and lecithin, stained with polychrome methylene blue, are sol. in acetone, alc., and benzine and are present both in "Wabenumgebung" and "Wabeninhalt" of both endoplasm and ectoplasm. A colored plate illustrates the color reactions. It is impossible to obtain any nuclear staining in the ameba by means of methyl green. This fact indicates the absence of nucleic acid and nuclein from the ameba. There is a detailed discussion of the physiological bearing of these facts. H. G.

**Chemical composition of some marine invertebrates.** F. BOTAZZI. *Ext. from Rept. Sci. Comm. on Nutrition, No. 10, of the Rend. accad. Lincei* 1920, pp. 16; *Physiol. Abstracts* 6, 113.—Analytical tables (water, dry residue, ash, org. substances, total N, and proteins) are presented of a marine alga (*Ulva lactuca*), certain invertebrates—*Phallusia mamillaris*, *Holothuria* (2 varieties), *Stichopus regalis*, *Cerianthus membranaceus*, *Sipunculus nudus*, *Eledone moschata*, *Octopus vulgaris*—and the flesh of the dog-fish (*Scylium canicula*). The total N in *Holothuria* is very high (11.5 and 12.7% of fresh material). The protein N is also high. The small amt. of proteins found in *Stichopus* and *Phallusia* is attributed to the high water content (90.43 to 94.76%). The protein of molluscs varies between 9 and 10.3%. The protein in the fresh muscles of *Scylium* is very high (17.43%); this number was obtained from material which had been previously extd. with an acidulated and concd. soln. of tannin. The number is higher than that of the total org. contents. B. explains this by pointing out that the muscles of

*Scyllium* contain other nitrogenous substances, which are probably pptd. by the acidulated tannin soln. together with the proteins. To obtain the exact amt. of the proteins contained in the flesh of *Scyllium*, as well as in the *Holothuria*, the material should be analyzed after extrn. with a reagent pptg. the proteins only. The ash of some of the marine invertebrates and of the *Ulva lactuca* is very high, but this is to be attributed to the fact that the body wall of such invertebrates and of seaweed in general contains many mineral substances; and as many of these are carbonates, which during incineration release  $\text{CO}_2$ , one must assume that the contents is ash registered in the table are somewhat less than the total amt. of mineral salts. H. G.

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The regulations for the examination of official government food chemists. HUGO SPIESS. *Chem.-Ztg.* 46, 405-6(1922).—German regulations are discussed. H. A. L.

Report on foods and feeding stuffs. J. B. REED. *J. Assoc. Official Agr. Chem.* 5, 418-20(1922).—The most satisfactory method for detg.  $\text{SO}_2$  in bleached grains is to treat the sample with phosphoric or tartaric acid, distg. and collecting the distillate in an acidified soln. of K iodate to which starch has been added. The method of Black and Alsberg (*C. A.* 5, 2407) for the detn. of acidity in corn is satisfactory for grains. Food products should be classified as to the method to be used in detg. moisture, as no one method is applicable to all substances. The methods of Reed (*C. A.* 16, 597) and Bisbee (*C. A.* 16, 597) for the detection of ground bran in shorts are not reliable for the inexperienced analyst. DOROTHY B. SCOTT

Notes on the examination of foods for the presence of sulfites. A. C. CHAPMAN. *Analyst* 47, 204-5(1922).—Foods and condiments which contain S in org. combination were found, when a weighed amt. was acidified with  $\text{H}_3\text{PO}_4$  and the distd.  $\text{H}_2\text{SO}_3$  caught in Br to have the S oxidized by the Br. If  $\text{H}_2\text{O}_2$  is used instead of Br only  $\text{SO}_2$  is obtained. This seems a convenient way to distinguish between volatile org. S compds. and  $\text{SO}_2$ .  $\text{H}_2\text{O}_2$  cannot be safely recommended to replace Br entirely, for when larger quantities of  $\text{SO}_2$  are in question there is not the same degree of certainty that the oxidation to  $\text{H}_2\text{SO}_4$  will be complete. LILLIAN OFFUTT

Method for determining hydrogen sulfide evolved by foods when cooked at various temperatures. E. F. KOHMAN. *J. Ind. Eng. Chem.* 14, 527-9(1922).—A method applicable at all temps. and to any volatile product which permits of steam distn. is described in detail.  $\text{H}_2\text{S}$  evolved when green corn was cooked at  $100^\circ$  and over was detd. gravimetrically as  $\text{BaSO}_4$ . Tables give the amt. of  $\text{KMnO}_4$  reduced by the distillate for variable conditions. DOROTHY B. SCOTT

Detection of artificial invert sugar in honey. S. F. SHERWOOD. *J. Assoc. Official Agr. Chem.* 5, 429-35(1922).—The literature on the resorcinol test for the detection of com. invert sugar sirup in honey is briefly reviewed. The results of the 4 collaborators show that neither the resorcinol nor the aniline-HCl test indicates the presence of the sirup in honeys heated at temps. that prevail in ordinary handling. A positive result indicates the presence of a foreign substance. DOROTHY B. SCOTT

Fitness of milk for cheese making. ROBERT BURRI. *Creamery and Milk Plant Monthly* 11, No. 6, 43-44(1922).—The fitness of milk depends upon normal chem. compn., certain phys. condition favorable to the process of cheese making and a bacteriol. condition characterized by the absence of injurious ferments. Therefore the milk producer must pay strict attention to the feeding and the physiological condition of the cows, clean milking app. and other hygienic conditions. H. F. ZOLLNER

Microorganisms in creamery butter. T. H. LUND. *Sci. Agr.* **2**, 332-40(1922).

E. J. C.

Does carbon dioxide in ice cream destroy bacteria? *Ice Cream Trade J.* **18**, No. 5, 49-51(1922); *Ill. Expt. Sta. Circ.* **256**.—The conclusions are: (1) CO<sub>2</sub> did not cause any appreciable reduction in the number of bacteria, (2) ice cream which had been inoculated with living typhoid bacteria and then carbonated in the usual commercial way showed typhoid bacilli after twelve days storage, (3) after exposure of several different types of milk bacteria in milk to CO<sub>2</sub> atm. the bacteria all continued to grow, (4) milk inoculated with typhoid and other bacteria was subjected to 10, 20, 40, and 60 lbs. pressure of CO<sub>2</sub> gas and under each set of pressures the bacteria continued to multiply.

H. F. ZOLLER

Fatty matters in "Uni." KATSUMI TAKAHASHI. *J. Chem. Soc. (Japan)* **43**, 243-57(1922).—Com. "Uni," salted sea-eggs, contains H<sub>2</sub>O 45.31, solids 54.69, total N 2.43, crude fat 12.91, crude ash 13.22, P 0.41%. Different lipins were sepd. by difference in soly. Lecithin and cephalin were identified by the N:P ratio:cholesterol by elementary analysis of the crystals. The fatty acids were sepd. by the usual Pb-soap method into unsatd. and satd. fractions. The fat contains per 100 parts: lecithin 19.628, cephalin 1.736, cholesterol 5.585, fat 73.051 in which 19.181 parts are satd. acids (mainly palmitic) and 53.870 parts are unsatd. Lecithin of Uni has N : P = 1 : 1.09, practically identical with that of egg yolk. Cephalin of Uni has N : P = 1 : 1.10, slightly higher than that of egg yolk of hens. Feedings expts. with rats show that Uni is rich in fat-sol. A.

Fat of "Kazunoko." KATSUMI TAKAHASHI. *J. Chem. Soc. (Japan)* **43**, 257-68 (1922).—Com. "Kazunoko," dried eggs of herring, contains H<sub>2</sub>O 8.32, solids 91.68%. The dried substance contains per 100 parts N 11.22, fat 14.22, crude ash 6.03, and P 0.54. The sample is well powdered, salt is removed by soaking in H<sub>2</sub>O, and dried till it contains about 1% H<sub>2</sub>O. It is then extd. with ether 5 times, and with alc. 4 times. By means of different soly. different fractions of the fat were sepd. Lecithin and cephalin were finally identified by N:P ratios, cholesterol by Liebermann and other color tests, and also by the m. p. of the crystals as well as elementary analysis. Dry Kazunoko contains lecithin 6.96, cholesterol 1.08, fat and oil 5.38%. Of the total fatty substance, lecithin is 48.95, cephalin 5.62, cholesterol 7.59, oil 37.84%. Of the fatty acids 24.87% are satd. (palmitic and stearic acid), and 75.13% unsatd. acids. Kazunoko contains fat-sol. A.

S. T.

Molds of frozen meats. BIDAULT. *Bull. soc. hyg.* **10**, 12-25(1922).—*Choetostylum fresenii* Van Thieghem, *Thamnidium elegans* Link Spee, *Penicillium crustaceum* Fries, *Hormodendron cladosporeoides* Bonorden, *Cladosporium herbarum* Link, *Stysanus stimoniles* Persoon, *Botrytis Micheli* and some varieties of *Eubotrytis* were isolated from frozen meat. From meat which had been thawed out after freezing and kept for a number of days at 15° in a dry atm., *Mucor racemosus* Fresenius, *Mucor spinosus* Van Thieghem, *Mucor mucedo* Linné and *Mucor pusillus* Link were obtained. Molds caused neither a decrease in nutritive value of frozen meats nor the formation of toxins although such meat had a disagreeable odor. As a prophylactic measure, preservation of the meats at -10° in a dry atm. is suggested with prompt fumigation of infected refrigerating rooms.

H. J. DEUEL, JR.

Report on crude fiber. G. L. BIDWELL. *J. Assoc. Official Agr. Chem.* **5**, 421-22(1922); cf. *C. A.* **16**, 594.—The proposed method as offered for adoption is as follows: Ext. 2g. of the dry material with ordinary Et<sub>2</sub>O, transfer the residue together with 0.5 to 1 g. of asbestos (previously digested on a steam bath overnight with 5-10% NaOH, washed with hot H<sub>2</sub>O, and digested overnight with 5-10% HCl, washed with hot H<sub>2</sub>O and ignited at bright red heat) to an Erlenmeyer flask, use a calibrated beaker add 200

cc. boiling  $\text{H}_2\text{SO}_4$  (1.25%) to the contents of the flask, heat on a battery using water-jacketed condenser (about 15 in.). The contents of the flask should come to boiling in 1 min. after being placed upon the battery. Boil 30 min., rotating the flask with the hand about every 5 min. Keep the sides of the flask above the soln. free from sample. Pass air blast into the flask to prevent frothing. After 30 min. remove the flask, filter in fluted funnel through linen ( $46 \times 50$  threads per in.) (such as to allow rapid filtration but to prevent solid matter from passing through). Wash until washings are not acid. Wash the charge back into the flask with 200 cc. boiling 1.25% NaOH using 200 cc. wash bottle. Boil for 30 min. as before. The boiling with alkali should be timed so that different flasks will reach the b. p. 3 min. apart to allow time for filtration. Filter into a Gooch crucible contg. a thin layer of the ignited asbestos. Use suction, wash thoroughly with hot  $\text{H}_2\text{O}$ , and then with about 15 cc. 95% alc. Dry crucibles to const. wt. at  $110^\circ$  in elec. oven, usually overnight. Weigh, incinerate in an elec. muffle or on a Meker burner at a dull red heat until carbonaceous matter is removed—20 min. usually—cool in a small light efficient desiccator and weigh. The loss is crude fiber. Discussion of points in this method is found in C. A. 16, 594.

LILLIAN OFFUTT

A study of the Gephart method for the determination of crude fiber. L. F. BOPST AND G. L. BIDWELL. *J. Assoc. Official Agr. Chem.* 5, 422-4(1922); cf. C. A. 16, 594.—The method used by Gephart (G.) is: Weigh 0.5 to 1 g. of the material into a special silica tube. Add 40 cc.  $\text{Et}_2\text{O}$ , stir, centrifuge 5 min. at speed of 3000 r. p. m. Pour off  $\text{Et}_2\text{O}$ , repeat. Dry tube and contents, add 40 cc. boiling 1.25%  $\text{H}_2\text{SO}_4$ , digest in boiling  $\text{H}_2\text{O}$  bath for 30 min. stirring frequently with glass rod with hooked end. Centrifuge 10 min., pour off liquid, add 40 cc. boiling  $\text{H}_2\text{O}$ . Stir, centrifuge 10 min., repeat. Add 40 cc. boiling 1.25% NaOH, digest 30 min. in boiling  $\text{H}_2\text{O}$ . Centrifuge as before. Wash twice with boiling  $\text{H}_2\text{O}$  and finally with 40 cc. of 50-50 mixt. of alc. and  $\text{Et}_2\text{O}$ . Dry at  $105^\circ$  to const. wt., ignite and weigh. Difference in wt. is crude fiber. The method was first used on cocoa and chocolate and was found to give slightly higher results than the proposed method. This is probably due to the removal of some of the material in the filtration after acid digestion which does not occur in the G. method. When tried on various feeding mixts. the higher the amt. of fiber present, the greater was the range of difference in the 2 methods. Samples of low fiber content, with the exception of flour, check fairly well. The G. method will be of value where samples have the texture of cocoa and spices which are difficult to filter without added asbestos. The proposed method, if adopted, will work with very little difficulty for any material.

LILLIAN OFFUTT

Self-rising flour—what is it? B. R. JACOBS. *Am. Food J.* 7, No. 5, 9-11(1922).—More than 25% of 37 samples of self-rising flour purchased on the market in the South were of inferior grade; only one contained as high as 11% gluten. Excess of phosphate or  $\text{NaHCO}_3$  was found in many samples. Regulation in the manuf. of self-rising flour is necessary as a health measure. Adoption of standards of purity for flour and leavening ingredients with limits in quantity of latter is recommended.

H. A. LEPPER

Valuation and separation of grains on the basis of the specific gravity. M. P. NEUMANN. *Z. ges. Getreidew.* 14, 2-9(1922).—The densities of most salt solns. are too low for the detn. of the d. of wheat. Mixts. of  $\text{CCl}_4$  and gasoline or petroleum of known d. are used and the wt. of grains which sink and float is detd. The d. of the grains can be titrated by adding the light liquid from a buret to the  $\text{CCl}_4$  contg. the grains and expressing the no. cc. necessary to make 25, 50, 75, 100% sink. There is a definite agreement (not numerical) between the wt. of a hl. and the d. of wheat grains, especially the titration values. The 1000 grain wt. showed some relation to the titration results. On the same sample the heavier portion has higher protein content than the lighter.

The heavier portion also has the higher hl. wt., greater 1000 kernel-wt. and greater content of large kernels. It appears to be possible to sep. the seed best for planting by means of liquid.

H. A. LEPPER

**Acme wheat.** A. N. HUME. South Dakota State Coll. of Agr. and Mech. Arts, *Bull.* 194, 327-58.—H. compares the yields of Acme with other grades of wheat. Tables are given showing moisture, protein and ash content of the various grades.

WM. HAZEN

**Report on stock feed adulteration.** H. E. GENSLER. *J. Assoc. Official Agr. Chem.* 5, 424-8(1922).—A method is given for the quant. detn. of grit and bone in poultry feeds and animal by-products. The results of 12 collaborators agree closely with the theoretical amts.

DOROTHY B. SCOTT

**Homegrown feeds for range steers.** Wyoming Agr. Expt. Sta., *Bull.* 128, 55-75 (June, 1921).—Contains tables giving chem. compn. of various kinds of hay, sunflower silage and other feeds.

WM. HAZEN

**Sun flowers: their culture and use.** Wyoming Agr. Expt. Sta., *Bull.* 129, 79-107 (June, 1921).—A treatise on the value of sunflowers for silage, with tables giving the compn. of sunflower and corn silage.

WM. HAZEN

The detection and determination of saccharin (POPPE) 7. Chemical kinetics of the system: reductase-methylene blue (YAMAZAKI, KANEKO) 2.

GERARD, E. and BONNE, A. *Traité pratique d'analyse des denrées alimentaires.* Paris: Vigot frères. 15 fr. Reviewed in *J. pharm. Belg.* 4, 35(1922).

PLIMMER, VIOLET G. and PLIMMER, R. H. A. *Vitamins and the Choice of Food.* London: Longmans, Green & Co. 164 pp. 7s 6d.

**Bread-making.** R. GRAHAM. *Brit.* 176,752, Oct. 12, 1921. Soy bean flour is used in making bread, the unpleasant characteristics being removed by baking a dough of soy-bean flour and bread materials with starch-decomposing and more especially diastatic addns. The enzymatic auxiliary substances may be added during the crushing of the beans or when the dough is being prepd., use being made, *e. g.*, of bran, malted grain, diastatic malt ext., or the suspension derived from flour of malted materials treated with warm or cold water and allowed to stand for several hr. in a cool room. Owing to the acid reaction of the crushed bean, the flour is desirably neutralized, before mixing it with the enzymatic auxiliary substances, with an alkali such as 1.5% of  $\text{NaHCO}_3$ . The soy-bean flour may be formed into an emulsion by dissolving it in weakly alk. boiling water, the emulsion being, if desired, freed from undissolved particles and mixed with the other ingredients. The dark brown bread produced is stated to resemble, according to the selection of materials, ginger bread or ordinary rye bread, and it has long keeping qualities and is easily digestible. Examples of suitable proportions of the various ingredients are given.

**Preparing yeast for food.** H. PLAUSON. U. S. 1,415,469, May 9. See *Brit.* 156,153 (*C. A.* 15, 1768).

**Powdered food from skim milk, chocolate, and sugar.** D. M. ANDERSON. U. S. 1,415,137, May 9.

**Preserving milk.** J. W. ROCHE, J. TAVROGES, L. O'BRIEN, H. TONGUE and G. MARTIN. *Brit.* 176,508, Dec. 8, 1920. In the manuf. of sweetened condensed milk, the milk is preheated and partly condensed, these operations being carried through very rapidly so as to affect the vitamins as little as possible; sugar is then added, and the condensation completed in a vacuum pan. In the process described, the milk is first heated

in a flash Pasteurizer to about 500°, and then evapd. in an app. of the type in which the milk passes upwards in a thin film along the inner surface of tubes heated externally by steam. The evapn. takes place at a temp. of 45–56° under a vacuum of 25–27 in. of Hg, and the milk is treated at about the rate of a gal. in 20 seconds for the two stages together. Sugar is then added, and the milk may be pasteurized. It is finally evapd. at about 120° F. for about 70 min. in a vacuum pan.

**Preserving milk.** J. W. ROCHE, J. TAVROGES and G. MARTIN. Brit. 176,509, Dec. 8, 1920. Milk to be condensed is preheated and then evapd., the two stages being rapidly so as to affect the vitamins as little as possible. In the process described, the milk is first heated in a flash Pasteurizer to about 50°; it then passes through an evaporator of the form wherein it passes upwards in a thin layer along the inner surface of tubes externally heated by steam. The milk is heated in the evaporator (cf. preceding pat.). The milk is reduced to rather less than a third of its original vol.

**Ice cream.** A. R. SANNA. U. S. 1,415,715, May 9. Milk for ice cream is treated to sep. the casein particles and enlarge them to a state approx. that of initial agglomeration and the treated milk is then homogenized.

**Ice cream.** L. H. P. MAYNARD. U. S. 1,415,669, May 9. An acidulated milk mixt. is mixed with an alkali cream emulsion, to improve the "smoothness" of the product.

**Butter fat.** C. E. NORTH. U. S. 1,416,053, May 16. Cream is agitated to effect agglomeration of fat particles and H<sub>2</sub>O is added of such a temp. as will liquefy the fat and cause it to rise and form a sep. layer.

**Curing, molding and packing cheese.** J. R. MEYERS. U. S. 1,415,942–3–4, May 16.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

**Instruction of students in the use of technical literature; an unexploited phase of engineering education.** E. H. McCLELLAND. *Eng. Education* 12, 407–20(1922).

E. J. C.

**Relation of employer and employee as regards ownership of patents.** MAURICE BLOCK. *Chem. Age* (N. Y.) 30, 201–2(1922).

E. J. C.

**Current chemical patents and patent problems.** LLOYD VAN DOREN. *Chem. Age* (N. Y.) 30, 235–8(1922); cf. *C. A.* 16, 1822.

E. J. C.

**Influence of patent law on the evolution of research.** H. E. POTTS. *Chem. Age* (London) 6, 726–7(1922).

E. J. C.

**Economics of power and heat in the chemical industry.** SARAZIN. *Z. Ver. deut. Ing.* 65, 382–7(1921).—A general discussion on heat economy. W. C. EBAUGH

**High temperatures in industrial processes.** P. W. FOSTER, JR. *Chem. Met. Eng.* 26, 458–62(1922).—Products may be heated up to 350° F. by using 150 lb. pressure steam in a closed coil or jacket. For higher temps. up to 600° F. the material is heated in a tank by means of a coil through which is circulated a mineral oil of high flash point, which has been passed through a directly fired heater, placed as close as possible to the tank in order to cut down radiation losses. Such losses if the equipment is well insulated should not exceed 10%. On this basis the efficiency would be about 63%, assuming complete combustion in the heater. The use of a circulating oil in this way has been in very common use for the last 10–12 years. Superheated steam provides another method which has been in successful use for the refining of vegetable oils which contain odorous constituents volatile at a high temp.; steam is blown through the liquid in a tank at the same time providing agitation. It is not practicable to use superheated steam in closed coils unless it passes through the coil at a high rate and can be utilized



after it has left the coil. This may be done by reheating and using in a series superheater. An efficiency of 75% may be obtained. Direct heating of materials which are easily charred is difficult because of local overheating. Of late this has been successfully accomplished by the use of special tubular heaters (drawing of which is shown) so designed that the tubes contg. the product are screened from radiant heat by special tile and cast-iron casings. Many vegetable-oil refineries are now using these heaters with more economy than when steam is used. The efficiency may reach 67 $\frac{1}{4}$ %. Roofing plants are now operating tubular heaters for heating asphalt coating.

A. C. LANGMUIR

**Recovery of radiated heat from a rotary kiln or drier.** ANON. *Chem. Met. Eng.* 26, 846(1922).—The kiln is to be surrounded by an insulated housing. Air is to be drawn through the annular space and thus preheated before being used in firing the kiln. The radiation from an uncovered kiln may be as high as 1000 B. t. u. per sq. ft. per hr. Insulation within the kiln is not practical because of the high temp. of the refractories which would result.

W. L. BADGER

**The relation between the composition of vapor and liquor in distillation.** E. PIRON. *Chem. Met. Eng.* 26, 317-20(1922).—A mathematical discussion of the fundamental laws governing the distn. of mixts. and the derivation of a number of formulas for use in practical distn., especially with ammonia liquor and mixts. of benzene and toluene. Reference must be made to a chart and tables.

A. C. LANGMUIR

**The evaporation of liquids in vacuum.** W. MASON. *Chem.-Ztg.* 46, 245-6, 290-1, 335-7, 354-6(1922); cf. *C. A.* 16, 1683.—Vapor velocities should not be over 100-150 ft. per sec. at 27 in. vacuum. Tests on a jacketed pan, 5 ft. 6 in. diam., walls 1.125 in. thick, 7 lb. steam, 27 in. vacuum, showed a coeff. of 30 B. t. u. per ° F. per sq. ft. per hr. during heating from 90° F. to 114° F., and 40 B. t. u. when evaporating. In a similar kettle lined with Pb 0.125 in. thick, the coeff. dropped to 10 to 12 B. t. u. Eight expts. are quoted on evaporators which are not specially described.  $a$  = number of expt.;  $b$  = type of evaporator;  $c$  = steam temp., ° F.;  $d$  = total temp. drop, ° F.;  $e$  = coeff. in B. t. u. per ° F. per sq. ft. per hr.;  $f$  = lbs. H<sub>2</sub>O evapd. per sq. ft. per hr.;  $g$  = lbs. H<sub>2</sub>O evapd. per lb. steam;  $h$  = % solids in feed;  $i$  = % solids in final product.

a.	b.	c.	d.	e.	f.	g.	h.	i.
1	single	233	95	114	10.8	0.81	39	56
2	single	201	68	112	7.6	0.82	28	52
3	single	216	83	215	18.	0.88	22	40
4	single.	270	130	123	16.	0.85	55	87
5	double	216	85	160	6.8	1.75	18	51
6	triple	204	79	228	6.	2.6	14	55
7	quad.	218	73	200	4.6	3.3	12	53
8	quad.	220	87	226	4.9	3.4	14	50

Air-pump capacity for an evaporator should be 5-7 lbs. air per 1000 lb. steam to 1st effect.

W. L. BADGER

**Condensation in self-ventilating tower coolers.** C. GRIBEL. *Z. Ver. deut. Ing.* 66, 31-6, 88-91(1922).—Expts. on a large scale were undertaken at works in Upper Silesia of the Silesian Electricity and Gas Co. in 1910-1914 to devise methods to cope with the growth of the plant. The results are illustrated in many charts, which enable the engineer to design a condensing system best fitted to the conditions prevailing.

A. C. LANGMUIR

**The recovery of volatile solvents by the Bayer process.** HANNS CARSTENS. *Z. anorg. Chem.* 34, Aufsatzteil, 389-92(1921).—Differing from the usual methods of condensation or absorption in liquids, a new recovery process was devised by Runkel during

the war utilizing the adsorptive power of highly porous charcoal. One cu. m. of this charcoal weighs 250 kg. and 1 kg. appears dry after adsorbing 500 cc. of any solvent.  $C_6H_6$  is completely adsorbed from a gas upon passage through this charcoal. Only above  $200^\circ$  can the  $C_6H_6$  be recovered by distn. unless a vacuum is employed. It is easily recovered, however, by passing steam through the charcoal. The pure solvent is recovered first, followed by a mixt. of steam and solvent. Solvents insol. in  $H_2O$  are thus easily sepd. directly, sol. ones by distn. The gas contg. the solvent is drawn through a vertical cylindrical container with a depth of charcoal approx. 1 m. As soon as the charcoal is satd., the gas is diverted to a new cylinder and a jet of steam blown through the satd. container. The condensed steam contg. the solvent is passed through a condenser. The charcoal is then dried with hot air, followed by cold air and is ready for further adsorption. The steam consumption is approx. 8 times the solvent recovered. Superheated steam is most economical, and by using steam at  $180^\circ$ , none is adsorbed and the drying operation can be omitted. The charcoal can be used indefinitely without deterioration. The velocity of the gas should not exceed 0.2–0.25 m. per sec. The satn. of the charcoal is best detected by the odor from an auxiliary outlet. The following dilns. can be detected in g. per cu. m.:  $CHCl_3$  0.0003,  $Et_2O$  0.001,  $AcH$  0.004,  $C_6H_{11}OAc$  0.09,  $MeOH$  0.6,  $EtOH$  5.75. The steaming, drying and cooling require 8–10 hrs. Comps. of low b. p., e. g.,  $MeCl$  can be recovered. Equipment and labor are comparatively low in cost.

C. C. DAVIS

**Asphyxiating gases.** E. VAN WAGENINGH. *Pharm. Weekblad* 59, 491–4(1922).—A brief description of the mfg. equipment at Edgewood Arsenal.

A. W. DOX

**Chemical warfare agents in the world war.** R. HANSLIAN. *Ber. pharm. Ges.* 31, 219–33(1921).—An account of the principal substances employed by both the Central and Allied powers during the late war, together with the manner and results of application, and methods for combatting same.

W. O. E.

**The elimination of industrial organic odors.** YANDELL HENDERSON and H. W. HAGGARD. *J. Ind. Eng. Chem.* 14, 548–51(1922).—A process is described for the elimination of industrial org. odors by admixture of the emanating gases with minute quantities of  $Cl$  gas. The amount of  $Cl$  required is detd. with quantitative accuracy. The process is used to advantage in chlorination of air, and in garbage disposal in cities. Application to the latter requires preliminary drying. The nature of odors and the use of deodorants are discussed.

W. H. BOYNTON

**The water-jacket method for testing gas cylinders.** H. E. SYRÖCKE. *Bull. Compressed Gas Manufs. Assoc.*, T. S. 1922, 152–7.—The water-jacket method for testing gas cylinders has the advantages of simplicity, rapidity, and past good service. Its disadvantages lie in the chances of error due to leakage from the cylinder, leakage from the jacket, presence of air in the jacket, variations in temp., difficulty of ascertaining the point of complete expansion, difficulty of differentiating between permanent metal stretch and rounding out, and failure to det. whether the yield point has been reached at the test pressure. The cylinder must be tested for leakage after the water-jacket test. The use of a permanent recorder in connection with this test is an improvement.

T. S. CARSWELL

**Notes on asbestos.** J. C. BROWN. *Bull. Indian Industries & Labor* 1922, No. 20, 31 pp.—Asbestos embraces several minerals which may be split into fibers capable of being spun or felted together, and are divided into two groups: Serpentine (chrysotile)  $3MgO \cdot 2SiO_2 \cdot 2H_2O$ , and amphibole. The latter group includes: Crocidolite,  $Na_2O \cdot Fe_2O_3 \cdot 2FeO \cdot 8SiO_2$ ; anthophyllite,  $(Mg, Fe)O \cdot SiO_2$ ; tremolite  $CaO \cdot 3MgO \cdot 4SiO_2$ ; and actinolite,  $CaO \cdot 3MgO \cdot 4SiO_2$  with some  $Fe$ . The numerous long-fiber asbestos deposits in India are unsuitable for the wide uses accorded serpentine, but should make good

insulation compns. for boilers, steam pipes, and fireproof paints. Uses of asbestos in general are outlined, the world's sources of supply discussed, and methods of dressing the fibers given.

W. H. BOYXON

**Insulating materials.** ANON. *Beama* 10, 374(1922); 17 illus.—Detailed directions for the study of hard composite dielectrics, as recommended by the British Elec. and Allied Industries Research Assoc. Elec. tests, mechanical tests and tooling characteristics are among the topics discussed.

C. G. F.

Failure of cast and high-silicon iron in fuming sulfuric acid (BANIGAN) 9. Lubricating oil from coal and crude oils (FREY, FABER) 22.

**Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry, 1921, Vol. VI.** London, E. C. 2: Society of Chemical Industry, Central House, 46-47, Finsbury Sq. Reviewed in *Chem. Weekblad* 19, 222(1922).

**Werkstoffe.** Handwörterbuch der technischen Waren und ihrer Bestandteile. Vol. II & III. Edited by Paul Kraus. Leipzig: J. A. Barth. 3 vols. combined M 450, bound M 540. Reviewed in *Z. angew. Chem.* 35, 188(1922).

**Effecting chemical reactions.** THERMAL, INDUSTRIAL & CHEMICAL (T.I.C.) RESEARCH Co., LTD. and J. S. MORGAN. Brit. 176,438, Nov. 2, 1920. Chem. reactions in solid, liquid, and gaseous substances, which are liable to disturbance by exothermic heating, are effected by heating the finely divided substance or mixt. of substances by passage through molten metal kept at a suitable temp.; by the rapid distribution of any locally developed heat to the molten metal, undesired secondary reactions are avoided. Examples of reactions to which the invention may be applied are the destructive distn. of wood, the oxidation of  $\text{CH}_4$  to  $\text{HCHO}$ , and, according to the provisional specification, the distn. of Ca acetate; thus, finely subdivided wood such as sawdust or shavings is fed to a bath of molten lead at  $350^\circ$  and caused to travel therethrough by a rotating drum or by means of a travelling endless band, as described in 174,974; a mixt. of  $\text{CH}_4$  and air or O is passed in the form of fine bubbles through molten metal heated to  $350\text{--}400^\circ$ , preferably in the still described in 170,617, (*C. A.* 16, 1119) the mixed gases being pumped into the hood and issuing therefrom as fine bubbles into the corrugations of the inclined plate.

**Cooling liquids.** J. BAKER, SONS, & PERKINS, LTD. and W. E. PRESCOTT. Brit. 176,469, Dec. 1, 1920. The evapg. and concg. app. described in 13,602, 1914 (*C. A.* 9, 3376) in which fluid to be concd., etc., is forced through a spiral passage surrounded by an annular steam jacket, is modified for use as cooling app. which may be used independently or in conjunction with the evaporator, in which case liquid is forced from the evaporator to the cooler by a pump. The cooler comprizes a stationary spiral baffle-plate forming a passage from the liquid to be cooled, arranged between 2 concentric tubular members, through each of which cooling fluid such as  $\text{H}_2\text{O}$  is circulated in a direction opposite to that of the fluid to be cooled. The outer member is of annular shape and the inner member is in the form of a tube closed at one end. Cooling liquid enters through pipes and leaves by pipes.

**Recovering condensable substances from gases.** E. SCHILL and F. WITTMICH. U. S. 1,415,058, May 9. Gases such as casing head gases from oil wells are cooled and compressed, expanded after devaporization and the expanded product is used to assist in cooling additional gas.

**Preventing evaporation of stored liquids.** F. A. HOWARD, C. I. ROBINSON and J. M. JENNINGS. U. S. 1,415,351-2, May 9. Liquids such as gasoline confined in

storage tanks are covered with a layer of permanent foam which may be formed from an aq. soln. of glycerol 10, gelatin 8, and  $\text{HgCl}_2$  0.1%.

**Purifying oils and solvents.** H. HAY. Brit. 176,540, Dec. 16, 1920.  $\text{H}_2\text{O}$  and fine solid suspensions are removed from used lubricating oils, from solvents after use in dry-cleaning, and from the solns. of oils, fats, and waxes obtained by treating bones, seeds, textile materials, etc., with volatile solvents, by intimately mixing with the cold solvent or hot oil a small proportion of sulfonated oils or sulfonated fatty acids, or of an aq. or alc. soln. of sulfonated oils or fatty acids or of their soda, potash, or  $\text{NH}_3$  soaps, and allowing the  $\text{H}_2\text{O}$  and solids to settle with the sulfonated oil. In an example 100 gal. of hot oil or cold solvent were mixed with 1 pt. of sulfonated oil or 2 pt. of the aq. or alc. soln. of the oil or soap, circulated for a few min. between a reaction and a settling tank, and allowed to settle. The sulfonated oil is produced by the action of strong  $\text{H}_2\text{SO}_4$  on oleic or ricinoleic acid or their glycerol esters or parent oils such as olive or castor oil, alone or mixed, and dissolved or not in gasoline, benzene, toluene, xylene, solvent naphtha, or other hydrocarbon solvent. The products may be washed with brine to remove free  $\text{H}_2\text{SO}_4$ , or neutralized with aq. or alc. alkali solns.

**Electric insulation.** W. H. KEMPTON. U. S. 1,416,036, May 16. A layer of material such as mica having high dielectric strength is placed between 2 layers of fabric impregnated with phenolic condensation product.

**Electrical insulating composition.** R. R. WILLIAMS. U. S. 1,415,076, May 9. Fused quartz and rubber are used for covering submarine cables.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

**W. P. Dunbar.** DR. KAMMANN. *Gesundh. Ing.* 45, 254-5(1922).—Obituary of Dr. W. P. Dunbar, Director of the Hygienic Institute of Hamburg for 29 yrs., and one of Germany's foremost Public Health authorities. MARTIN E. FLENTJER

**Report of the water-softening and purification works for the year 1921.** CHAS. P. HOOVER. *City Bull.* (Columbus, Ohio) 7, No. 16, 12-21(1922); cf. C. A. 15, 3352.—7,936 mil. gal.  $\text{H}_2\text{O}$  were softened (lime-soda) during 1921 to an av. hardness of 100 p. p. m. There was an av. reduction in bacteria from 2450 to 24 per cc.; there were 10 deaths from typhoid fever during the yr. (population city 247,000). Operating results are included. G. C. BAKER

**Report of the American Committee on electrolysis 1921.** V. B. PHILLIPS. *J. Am. Water Works Assoc.* 9, 449-54(1922).—A summary of the subjects covered with some quotations from the report which the article reviews. D. K. FRENCH

**The purification of turbid water for use in boilers.** ANON. *Wärme u. Kälte Technik* 24, 81(1922).—A brief description of purification by pptn., settling, and filtration. ERNEST W. THUELE

**Removal of bacteria by zeolitic water softeners.** G. C. BAKER. *J. Am. Water Works Assoc.* 9, 474-87(1922); *Fire & Water Eng.* 71, 245-6, 248, 251.—Contrary to the generally accepted idea, zeolitic water-softening filters do not quantitatively remove *B. coli*. Such removal as is effected is purely mech. Of the filters tested Borromite seemed to possess a slightly higher efficiency than the others. D. K. F.

**Long record of microscopical examination.** GEO. C. WHIPPLE. *J. Am. Water Works Assoc.* 9, 436-41(1922).—A record of microscopic organisms in Wachusett Reservoir, etc., for 22 yrs., which indicates the ultimate necessity of filtration. D. K. F.

**Physical chemistry of deferrization.** R. S. WESTON. *J. Am. Water Works Assoc.*

9, 491-5(1922).—Discusses the steps in deferrization, *i. e.*, aeration and removal of acid, hydrolysis and coagulation. D. K. FRENCH

Applied hydrogen-ion concentration. Study of its merits in practical filter-plant operation. A. WAGNER AND LINN H. ENSLOW. *J. Am. Water Works Assoc.* 9, 373-91 (1922).—As a result of extended investigation the Tillman formula is considered satisfactory for practical purposes, save where alk. exceeds 65 parts for each part of free  $\text{CO}_2$  present. Direct  $p_{\text{H}}$  observations are not always necessary. Control of artificial alk. and reduction of  $\text{CO}_2$  should be limited. Coagulation is improved by the introduction of inert material as limestone, finely ground sand, etc. Other methods of control are discussed whereby economy and efficiency in coagulation and filtration are obtained. Some further work is suggested. D. K. FRENCH

Investigation of the Elbe River water at Magdeburg and Hamburg. OTTO WENDEL. *Z. angew. Chem.* 35, 219-23(1922); cf. *C. A.* 15, 2320, 2946.—The 1922 report of the Elbe River investigations compares the av. monthly sanitary analyses of 1921, and the av. yearly analyses since 1912. From the data obtained W. concludes: (a) the river water in 1921 did not show any great difference in salt concns. from the preceding yrs., the difference shown being accountable for by low water; (b) the salt concn. is dependent on the stage of the river; (c)  $\text{NH}_3$ ,  $\text{HNO}_2$ , and  $\text{HNO}_3$  are never present in more than traces; (d) the concn. of the org. compds. is greater in winter, during low water and in the presence of ice. MARTIN E. FLENTJE

Chlorine tastes and odors from pipe coating. E. J. ROWE. *J. Am. Water Works Assoc.* 9, 455-7(1922).—Another case (cf. *C. A.* 16, 1475) where Cl-treated water in a coal tar-treated pipe developed objectionable phenol- and iodoform-like odors and tastes. D. K. FRENCH

Causes of obnoxious tastes and odors sometimes occurring in the Cleveland water supply. J. W. ELLMS AND W. C. LAWRENCE. *J. Am. Water Works Assoc.* 9, 463-73 (1922).—Waste mfg. products discharged into the Cuyahoga River are under certain conditions carried to the water-supply intakes. This is especially true when ice is on the lake. Waste products from the distn. of coal and gas liquors are especially objectionable. D. K. FRENCH

Cleveland water system. G. E. FLOWER. *J. Am. Water Works Assoc.* 9, 418-25 (1922).—The supply is taken from Lake Erie. Since 1911 Cl in some form has been used.  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{FeSO}_4$  are used in connection with filtration. Full details of the plant equipment are given. D. K. FRENCH

Measurement of water supply by the Pitot tube in Syracuse, N. Y. H. R. STARBIRD. *J. Am. Water Works Assoc.* 9, 403-7(1922).—Nine Simplex Pitot recorders are now in use and giving excellent results. D. K. FRENCH

Solution of corrosion and coagulation problems at Montebello filters, Baltimore. J. R. BAYLIS. *J. Am. Water Works Assoc.* 9, 408-17(1922).—The use of alum as coagulant frequently increases the corrosive qualities of a water. Lime properly applied after filtration rather than before will reduce and frequently eliminate this type of trouble. A large amt. of detailed work is recorded. D. K. FRENCH

Cement gun in water works practice. L. R. TALBOT. *J. Am. Water Works Assoc.* 9, 446-8(1922).—The cement gun using Gunitite is especially satisfactory in water works practice as the coating so produced is more dense than that obtained by ordinary methods, and when properly placed makes a water-tight job. Several instances of its use are given. D. K. FRENCH

The use of chlorine gas in the purification of sewage. J. TILLMANS. *Gesundh. Ing.* 45, 255-50(1922).—T. reports the results of a no. of expts. on sewage treated with varying amts. of Cl gas ranging from 3-20 mgs. per l. Conclusion: By the addn. of but small

amts. of Cl gas; (a) the rate of decompn. of the sewage material can be greatly decreased, (b) the acid concn. can be kept nearly const., (c) nitrate decompn. will take place more slowly, (d) the formation of  $H_2S$  takes place much more slowly and in smaller quantities, and (e) the high mol. albuminous compds. present will also decompose much more slowly. T. therefore recommends the use of Cl gas where a relatively large amt. of sewage must enter a small dilg. stream, in order so to decrease the rate of decompn. that it will not become objectionable before reaching a larger body of water. M. E. F.

**Grease production by the action of fly larvae on sewage, as a means of sewage and waste purification.** HERMANN KOSCHMIEDER. *Gesundh. Ing.* 45, 259–60(1922).—After a brief résumé of the common methods of sewage purification and waste utilization, K., from the publications of Lindener (Grease production by bacteria, *Z. tech. Biol.* 7(1919) and The Problem of grease formation, *Kraft, und Stoff*, Mar. 25, 1922), suggests that fly larvae may offer a means of solving the utilization problem of sewage. Considerable research on methods and control conditions would be necessary.

MARTIN E. FLENTJE

**Cross gradients and the drainage of city streets.** FEURER. *Der städtische Tiefbau* 1922, 17ff; cf. *Gesundh. Ing.* 45, 239(1922).—Formulas and tables are given for the draining of public streets, based partly on experiences in Frankfurt. M. E. F.

**Disinfection with hydrocyanic acid.** WOLF. *Pharm. Ztg.* 67, 316(1922).—The danger incident to the use of HCN is emphasized in the disinfection of buildings. "Zyklon" ( $CNCO_2Me$ ) is regarded as less objectionable in this respect. Nevertheless, the promulgation of a law prohibiting the use of HCN and its derivatives is shortly expected.

W. O. E.

The elimination of industrial organic odors (HENDERSON, HAGGARD) 13. Apparatus for separating gases from liquids (U. S. pat. 1,416,632) 1.

PURVIS, J. E. and HODGSON, T. R.: **The Chemical Examination of Water, Sewage and Foods, etc.** 2nd Ed. revized. Cambridge: University Press. 20s. Reviewed in *Chem. Trade J.* 70, 600(1922).

**Artificial ice.** R. ELLIS. U. S. 1,415,325, May 9.  $H_2O$  to be frozen is treated with a readily adsorbed material such as saponin, 0.0001% or less, to inhibit the freezing of air bubbles into the ice.

**Apparatus for aerating and purifying sewage.** J. P. BALL. U. S. 1,415,007, May 9.

**Garbage treatment.** C. G. ARMSTRONG. U. S. 1,415,290, May 9. Garbage is satd. with a hydrocarbon such as kerosene to act as a deodorant and solvent and is afterward transferred to a reduction plant where it may be treated with additional hydrocarbon oil and heated to sep. oils, grease and  $H_2O$ .

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

**Fortieth annual report.** Ohio Agr. Expt. Sta., *Bull.* 353, 1–30 pp.(June, 1921).—Brief reports are given of work on P availability in soils, in relation to soils and crops, K supply of the soil, and influence of silicates on the growth of plants. W. H.

**Revival of arable land.** A. PETIT. *Compt. rend.* 174, 1033–4.—P. claims priority over A. Lumière in the record of the observation that ordinary garden soil repeatedly extd. with distd. water shows a more rapid growth of plants than the same soil merely moistened with distd. water. (Cf. Petit, *Principes gen. de la culture des plants en pots*, 1909, p. 60 and A. Lumière, *Compt. rend.* 171, 868–71(1920).) L. W. RIGGS

**Spent sulfite liquor as a fertilizer.** H. G. SÖDERBAUM. *Centralanstalten för öfversändel jordbruks Medd.* No. 230, *Kemiska advel* No. 33, 12 pp. (1922).—The neutralized sulfite liquor contained 19.4% org. matter, of which 4–5% was sugar. The inorg. content was 3.5%, of which 0.03% was K. No phosphoric acid was present and the N content was only 0.02%. Expts. were carried out with oats on a poor sandy soil. The containers held about 30 kg. of soil, to which a basic fertilizer of phosphate,  $\text{CaSO}_4$  and  $\text{NaNO}_3$  was added. Sulfite residue was added in increasing amts. from 12.5 to 100 cc. per vessel. The results showed only in a few cases an increased yield of about 10%. No harmful effects were observed with even the largest amts. of sulfite liquor.

C. E. CARLSON

**Influence of barnyard manure on the decomposition of cellulose in the soil.** C. A. G. CHARPENTIER. *Central anstalt. försöksväsendet på jordbruks. Medd.* No. 218, 1–41.—Clay, sand and peat soils were used in 1-kg. amts., placed in containers closed with stoppers in each of which was a glass tube filled with cotton. The materials were added to the soils in these amts.: Cellulose 1%; manure 2%;  $\text{CaO}$  0.5% as  $\text{CaCO}_3$ . There were controls for each of these. The source of cellulose was filter paper, cut fine. The mixts. were made up to the optimum moisture content and this as well as the temp. was kept const. The amt. of undecomposed cellulose was detd. from time to time. (Cf. C. A. 15, 3167.) The manure greatly increased the rate of decompn. of cellulose in the clay and sandy soil, but had little influence in the peat soil. The influence of lime was on the whole small. More molds developed in the absence of lime. The greater the amt. of moisture, provided the air is not excluded, the greater the decompn. of cellulose. The effect of manure is due primarily to its supply of nutrients which favor the development of cellulose-decomp. organisms, and the most important nutrient is nitrogen. This was shown by the use of  $(\text{NH}_4)_2\text{SO}_4$ , which gave a curve parallel to that of manure.

C. O. SWANSON

**Effect of fertilizers on quality of the potato.** A. KRAFT. *Forschungsinst. Kartoffelbau* 1920, No. 3; *Physiol. Abstracts* 6, 161.—Com. potash fertilizers, when applied singly, are usually toxic to the potato on account of the chloride they contain. Fertilizing only with nitrogenous fertilizers increased the protein, but decreased the ash content; the plants grow well and are dark green. The influence of phosphates depends on the concn. and form of the lime presented to the plant. Stable and green manure influence the potato favorably.

H. G.

**Effect of fertilizers and lime on control of tomato leaf spot (*Septoria lycopersici*).** F. J. PRITCHARD AND W. E. PORTE. *Phytopathology* II, 433–45 (1921).—Tomato plants inoculated with *Septoria lycopersici* were grown in glasses and pots receiving applications of  $\text{NaNO}_3$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{CaH}_4(\text{PO}_4)_2$ , lime, and  $\text{CaSO}_4$  to det. their effect on the control of tomato leaf spot. None of the materials used increased or decreased the susceptibility of the tomato plants to leaf spot except as it affected growth, or the internal conditions affecting growth. This was also true of the different ratios or quantities of fertilizers used. Treatment with these substances either increased or decreased the leaf area and thereby caused a corresponding alteration of the no. of infections per plant.

J. J. SKINNER

**Graphitic nature of the carbon of lime-nitrogen (KAMEYAMA) 18.** Silicon nitrogen compounds [for fertilizers] (U. S. pat. 1,415,280) 18.

**Zeitschrift für Pflanzenernährung und Düngung.** A-Wissenschaftlicher Teil. B-Wirtschaftlicher-Praktischer Teil. *New Journal* A 6, B 12 times a year. Leipzig: Verlag Chemie G. m. b. H., Nürnbergerstrasse 48. A \$3, or M 48. B \$4 or M 60, A & B \$6 or M 100.

**Insecticide.** M. L. Tower. U. S. 1,416,526, May 16. Nicotine sulfate soln. is mixed with a dehydrating agent such as plaster of Paris and with an arsenate, tobacco-dust and finely divided S.

**Insecticide.** KYŌJI KUWAZUKA and MITSUBISHI KŌGYŌ KABUSHIKI KAISHA (Mitsubishi Mining Co.). Japan 39,165, July 6, 1921. A mixt. of  $\text{CuSO}_4$  1 and concd.  $\text{NH}_4\text{OH}$  2 parts is thoroughly mixed with 4 parts concd. soap soln. In some cases petroleum or As compd. is mixed with the emulsion.

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

**The alcohol question.** E. RABBETHGE. *Chem.-Zig.* 46, 429-30(1922).—Recommends the use of potatoes for the production of alc., for if potato production is thus stimulated, the amt. available for food will also be increased. C. N. FREY

**Can the extent of alcohol production be made dependent on the disposal of alcohol?** F. HAYDUCK. *Chem.-Zig.* 46, 389-90(1922).—The alc. industry in relation to the restrictions imposed by the government on the use of raw material is discussed, and an outline for future development is given. C. N. FREY

**The manufacture of alcohol from molasses.** E. HUMBOLDT. *Louisiana Planter* 68, 205-8(1922).—The mash is best prepd. by dilg. the sterilized molasses to 12-18° Bx., adding nutrients, such as  $\text{NH}_4$  salts and antiseptics, alk. sulfites, fluorides. Pure cultures of yeast give larger yields of alc. Cultures may be started from the individual cell and acclimated to the type of mash used. The processes of fermentation and sedimentation require 3 days and secondary fermentation is then carried on. Scrubbing of the escaping gas from the fermentation tubs permits a saving of alc. The rectification of alcohol is carried in, in modern stills. The theoretical yield from dextrose is 51.1% and from sucrose 53.8%, with 83% recovery as good practice. C. H. C.

**Production of glycerol by fermentation.** BODE. *Z. Spiritusind* 42, 140-1(1919); *Abstracts Bact.* 4, 116.—A review of the progress made in Germany in the manuf. of glycerol through alc. fermentation. The advantage of using  $\text{Na}_2\text{SO}_3$  and an alk. soln. is pointed out. With an increase of sulfite there is an increase in the amt. of glycerol to a max. of 27.1%, a decrease in the production of alc. from 40% to 23.3%, an increase in aldehyde from 2.4% to 8.6% and a decrease in  $\text{CO}_2$  from 37.8% to 29.4%. H. G.

**Glycerol production by fermentation.** BODE. *Wochenschr. Brauerei* 42, 13(1919); *Abstracts Bact.* 4, 116; cf. preceding abstr.—The addn. of alkali in amts. not damaging to the yeasts increased materially the amt. of glycerol formed in alc. fermentation.  $\text{Na}_2\text{SO}_3$  exerts a particularly favorable influence. On the other hand, the kind of yeast, the character of the sugar and the fermentation temp. do not have an appreciable effect on the formation of glycerol. In some tests as much as 15% of glycerol was produced in fermenting fluids in which yeast had access only to sugar and mineral salts. On a large scale, one may obtain from 100 parts of sugar 20 parts of glycerol, 27 parts of alc. and 3 parts of aldehyde. The yeasts remain active in spite of some slight morphological changes and in spite of the high concn. of salt and the strong alk. reaction of the nutrient soln. They may be used for inoculation of succeeding vats. The appearance of aldehyde in addition to alc. is characteristic. The amts. of aldehyde and glycerol increase with the addn. of the sulfites while the amts. of alc. and  $\text{CO}_2$  decrease. H. G.

**Detection and determination of vanillin in spirits.** TH. VON FELLENER. *Mitt. Lebensm. Hyg.* 13, 98-110(1922).—Vanillin is detd. by sublimation and by colorimetric methods. C. N. FREY



**Critical study and new contribution on the analysis of brandy.** G. BONIFAZI. *Mitt. Lebensm. Hyg.* 13, 69-95(1922).—Gives methods for distinguishing natural from artificial brandies. C. N. FREY

**A process for the determination of individual acids of wine—percentage composition of constituents of wine and cider.** TH. VON FELLNBERG. *Mitt. Lebensm. Hyg.* 13, 1-45(1922).—Methods for the detn. of malic, tartaric, lactic, succinic, tannic and phosphoric acids in wines and ciders are given. C. N. FREY

**The composition of wine from lees and of lees from wine.** L. SEMICHON. *Compt. rend.* 174, 1179-82(1922).—Comparative analyses of 3 grades of wine are given. C. N. FREY

**The filtration of wines.** L. MATHIEU. *Chimie et industrie* 7, 669-72(1922).—Wines can be clarified by sedimentation, centrifuging, coagulating colloids (albumin, etc.) in the wine, or by filtration. Includes discussion of factors involved. A. P.-C.

**The vinification of tropical fruits.** PIQUE. *Bull. assoc. chim. suc. dist.* 39, 274-9(1922); cf. C. A. 16, 784.—A method for making wine from sugar cane and the results of some expts. on the production of alc. from various species of sweet potatoes are given. J. D. GARARD

**Preparing yeast for food** (U. S. pat. 1,415,469) 12. **The sugar and distillation industries in Brazil** (DESMET) 28.

**Extracting glycerol from weak solutions obtained by fermentation.** E. A. BARBET. U. S. 1,416,318, May 16. Weak liquors contg. glycerol are partially concd. and then subjected to a further concn. by circulation and energetic heating in an evaporator and fractional distn. in a column still under reduced pressure.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**Experimental chemotherapy and the future status of medicinals in the patent law.** W. EICHHOLZ. *Z. angew. Chem.* 35, 205-6(1922).—E. discusses the conditions of the present exclusion of medicinals from the protection of the patent law and the possible future developments in this field. JAMES A. BRADLEY

**The cinchona barks of the Dutch East Indies.** A. GROOTHOFF. *Chimie et industrie* 7, 792-806(1922).—A review of the establishment of cinchona plantations in Java and Sumatra, their development and present status, with a description of *Cinchona ledgeriana* (Moens) and of *C. succirubra* (Pavon), of the prepn. of quinine, and an analysis of the status of the quinine and cinchona bark trades. The following method is used at the quinine testing lab. established by the planters, for the detn. of cinchona alkaloids in *C. ledgeriana*. Ext. with ether a mixt. of the well ground bark with  $\text{Ca(OH)}_2$ , NaOH solns. Det. total alkaloids by dissolving the  $\text{Et}_2\text{O}$  residue in  $N$  HCl and titrating with  $N$  NaOH, with litmus as indicator. Ppt. tartrates of quinine and cinchonidine, filter, wash, dry, and weigh. Det.  $\alpha$  and calc. quinine and cinchonidine from Cammellin's table (Memoir No. 1 of the Quinine Testing Station of Java). To the filtrate from the quinine and cinchonidine tartrates add NaI soln. to ppt. quinidine, cinchonine, and amorphous alkaloids; sep. the quinidine by means of 94% alc. Cinchonine alone is very seldom detd. The quinine sulfate content found by this method averages about 0.2% lower than that found by the method of the govt. plantations lab. A. P.-C.

**Oswald Schmiedeberg.** ANON. *Naturwissenschaften* 10, 105-7(1922).—An obituary. C. C. DAVIS

**Suppression of the ten per cent tincture of iodine of the French pharmacopeia.** ANON. *Répert. pharm.* 34, 101-5(1922).—Tincture of I of the French Codex of 1884 contained 10 g. of I in 120 g. of 90% EtOH. In the Codex of 1908, the formula was changed to 10 g. in 90 g. of 95% EtOH to make it conform to the formula adopted by the Brussels Conference. Owing to complaints of the caustic properties of this stronger tincture, a formula for a less active prepn. was included in the Supplement to the Codex issued in 1920 under the title *Teinture d'iode iodurée*. This formula called for 10 g. of I and 4 g. of KI in 136 g. of 90% EtOH. As a result of a recent fatality due to confusing these two prepn.s, the Minister of Public Instruction issued a decree suppressing both tinctures and making official a new prepn. contg. 10 g. of I and 4 g. of KI in 140 g. of EtOH. This prepn. bears the title *Teinture d'iode officinale*. A. G. DuMaz.

**Decree relative to the modifications and additions to the French pharmacopeia.** ANON. *Rept. pharm.* 34, 129-35(1922).—In the interval between the publication of editions of the French pharmacopeia, the following additions, deletions and changes have been made effective by a decree published in the official journal. **Additions.**—Colloidal Ag prepd. by chem. means, diacetylmorphine-HCl, emetine-HCl, ethylmorphine-HCl, potassium guaiacolsulfonate,  $\text{NaBO}_3 + 4\text{H}_2\text{O}$ ,  $\text{ZnO}_2$ . **Deletions.**—“Teinture d'iode” and replace with “Teinture d'iode officinale.” Monographs for each of the foregoing are given as well as an assay method for the new tincture of iodine. For details the original article should be consulted. A. G. DuMaz.

**Higher aliphatic aldehydes and alcohols.** G. PRINZ. *Am. Perfumer* 17, 122a-122b(1922).—P. enumerates the aldehydes and alcohols most important to the perfumer, the oils from which they are obtained, and the combinations in which they are most properly applied. W. O. E.

**Does the percentage of esters correspond to the best perfume value and yield for a lavender oil?** G. BLANC. *Am. Perfumer* 17, 122c(1922).—The bouquet or perfume value and the yield of a lavender oil are entirely different matters. The yield of a lavender oil is given approx. by its ester value. In order that the amt. of ester should be a measure of the value of an oil, it is most important that the oil be pure, deprived of any artificial esters. It must have been distd., besides, under special conditions to reduce to a minimum inodorous and resinous parts testing as ester. W. O. E.

**Examination of B. P. ointments.** N. EVERS AND G. D. ELDON. *Analyst* 47, 197-202(1922).—A number of methods or modifications of existing methods have been devised, and outlines of these are given under the various headings. Some 15 different ointments were examd. Since ointments contg. a volatile constituent are liable to lose a certain proportion of such ingredient in the course of their prepn., expts. were carried out with this point in view. In phenol and salicylic acid ointments the losses in prepn. may amount to 30 to 40%, while with creosote and eucalyptus prepn.s the losses are around 10%. Detns. of  $n_{50}$  of certain ointments showed that this value does not except in a few cases give much information as to the strength of the active constituent present. W. O. E.

**Determination of alkaloids.** P. HERZIG. *Arch. Pharm.* 259, 249-308(1921).—In the present paper the author has undertaken to assemble and arrange the numerous methods heretofore suggested for the detn. of the alkaloidal constituents of crude drugs and their products. Gravimetric, volumetric, colorimetric, refractometric and polarimetric procedures are critically considered in the order named. W. O. E.

**Determination of cresol in cresol soap solutions.** L. FRANK. *Chem.-Zig.* 46, 390(1922).—Since the evaluation of the official cresol soap soln. according to the method specified in the Ger. Pharm. is somewhat cumbersome and subject to error, F. recommends a new procedure, involving a special type of Erlenmeyer flask (having a graduated test-tube-like cylinder melted into the base), whereby the exptl. error is reduced to about 1%. W. O. E.

**Rose otto from rose flowers (*Rosa damascena*) of the United Provinces.** S. T. GADGE AND B. C. MUKERJI. *J. Indian Ind. Labour* 2, 86-102(1922).—Rose flowers grown for purposes of distn. in certain districts are superior to those available at Cawnpore or Ghazipur. With preservatives like NaCl the flowers can be stocked undamaged for distn. purposes for 3 or 4 days after plucking. The superiority of the roses from the Aligarh district appears to be due to the richer soil and better irrigation. The high results in the yield of otto reported by the Indian Essent. Oils Co. last year could not be verified, the av. obtained not exceeding 0.015%. The optimum yield obtainable is much below the Bulgarian figure. Detn. of the I absorption value of rose H<sub>2</sub>O as described in this report appears to be a ready and reliable means of evaluating this commodity in terms of otto. The types of still tested involved the Deg, Bulgarian and steam stills; all gave similar results with a given variety of flowers. Live steam is unsuited for making otto from rose flowers. A steam-jacketed still would be ideal, but its use may not be practicable on rose fields and with all grades of distillers. A 4th type of still tried was a modification of the Deg with a separable top, contg. a fairly wide leading tube with which could be connected a worm condenser when the still was in operation. It is portable and offers easy working. W. O. E.

**Monographs on floral odors. X. The violet group, civet and ambergris.** P. P. R. *Perfumery Essent. Oil Rec.* 13, 151-3(1922); cf. C. A. 16, 3196.—Under the violet group attention is given acacia, mimosa, cyclamen, iris, kostus and mignonette, especially their perfume-giving ingredients. Civet and ambergris are described in considerable detail. The paper includes working formulas for producing both the basic and flower oils. W. O. E.

**Hypotonin.** T. SABALITSCHKA. *Pharm. Ztg.* 67, 327(1922).—This prepn. occurs both in powder and tablet form; it consists of ethylenediamine isovalerate, m. 129-30°. Several identity tests are given. W. O. E.

**Odor value analysis.** W. G. UNGERER AND R. B. STODDARD. *Ungerer's Bull.* 3, No. 1, 7-10(1922).—A theory of odor and odor values, substantially as follows is presented: Odor is the response of the olfactory nerves to inter-mol. vibrations, which the most delicate instruments yet devised can hardly detect, much less record and measure. Every pure substance has its own rate of vibration, which may be such as to influence the olfactory nerve and produce the sensation of odor or it may be too low or too high to be detected at all, just as certain ether vibrations are outside the range of the eye and ear. The theory is supported by the fact that practically all substances having perceptible odor are unsatd. in the chem. sense, such substances being most subject to inter-mol. movements and vibrations which are assumed to give rise to the phenomenon of odor. It becomes the problem of the perfumer so to compound substances as to produce a definite and desired odor sensation; to do so he must combine those vibrations in such a way as to produce a definite rate or sort of vibration, not so unlike the inter-effects of sound and color vibrations of varying wave length. An odor may be profoundly modified by the addition to the perfume of an almost inappreciable amt. of a substance which of itself does not possess a powerful odor. The effect produced by the added substance is due to the perfect coördination of its vibrations with those of the compn., the composite vibration affecting the olfactory nerve in the desired way. Many substances gradually lose their supposedly characteristic odor and become almost odorless as they approach a state of absolute purity. Yet when the so-called impurity is isolated in appreciable amt. it is found to have a characteristic but not particularly powerful odor, which tends to disappear as the substance approaches the unattainable limit of absolute purity. This can be explained by the new theory of odor. If this theory of odor value is essentially correct there can be little doubt that today our perfume compositions waste the major portion of the odor value of the constituents, which to a large

degree merely nullify each other. A study of odor values on the basis of this theory will require the utmost refinement of scientific work, and the invention of new and wonderfully delicate instruments, and it will mean that perfume materials must be prepd. in a far higher degree of purity than has ever before been attempted. W. O. E.

Oil sassafras, natural. R. M. DUDLEY. *Ungerer's Bull.* 3, No. 1, 19-20 (1922).—The production of the oil is described in detail as practiced in the southern states. A pure high-quality oil sassafras should have a d. close to 1.070 at 25°, and a + optical rotation slightly above 2°. W. O. E.

Gum resin of the Euphorbia tirucalli. L. RAYBAUD. *Compt. rend. soc. biol.* 83, 1442-4 (1920); *Physiol. Abstracts* 6, 223.—An analysis of the gum is given. H. G.

Some incompatibilities of newer remedies. A. RUDDIMAN. *Boll. chim. farm.; Schweiz. Apoth. Ztg.* 60, 236-8 (1922).—The remedies discussed are agurin, alumnol, ammonol, eutrophenum, phenocoll-HCl and ichthyol. S. WALDBOTT

The French Codex, second Supplement. ANON. *Chemist and Druggist* 96, 655-6 (1922).—Collargol, heroine-HCl, emetine-HCl, dionin, thiocol, Na perborate and Zn peroxide have been added, and tincture of I has been replaced by an iodized tincture of I: I 10 g., KI 4 g., 90% EtOH 136 g. S. WALDBOTT

Tincture of iodine-iodide. H. MARTIN. *J. pharm. chim.* 25, 198-202 (1922).—A discussion of the poisonous character of old tincture of iodine, and the necessity of officially replacing this prepn. by tincture of I-KI. S. WALDBOTT

Some technical points in the method of physiological control of adrenaline products. A. RICHAUD. *J. pharm. chim.* 25, 289-98 (1922); cf. *C. A.* 15, 2336.—The necessity of washing the adrenaline (A) from the cannula after each injection by Cushny's control method is discussed. From the tracings obtained upon injecting for comparison solns. of unknown and known strengths of A, R. deduces the increase of blood pressure (which is a function of the adrenaline contents), by drawing the heights of the curves. A graph made from these increments as ordinates and the concns. of the solns. used as abscissas, gives a direct means of comparison. S. WALDBOTT

Determination of arsenic in some medicinal chemicals. J. CRIBBER. *J. pharm. chim.* 25, 337-40 (1922).—The As content in 48 different chemicals is detd. by C.'s method (*C. A.* 15, 35). Sb and Fe and some of their compds. contain the largest amts. To det. As in compds. of Sb, Fe and Bi, sep. the As from these by pptg. it as  $MgNH_4AsO_4$  together with a ppt. of  $MgNH_4PO_4$  produced in presence of tartaric acid. S. WALDBOTT

An examination of chemical food. A. J. JONES. *Pharm. J.* 108, 61-2; *Chemist and Druggist* 96, 116 (1922).—This substance, *Compd. sirup of ferrous phosphate*, Brit. Pharm. Codex, needs revision of its formula; its acidity (3.07% free  $H_3PO_4$ ) is too high. In 5 com. samples, the free, "associated" (with  $Ca_3(PO_4)_2$  and  $Fe_3(PO_4)_2$ ) and the total,  $H_3PO_4$  are detd. and compared with the B.P.C. standard. These detns. are based on the following reactions: When titrating pure  $H_3PO_4$  with NaOH, Me orange (M) detns. the 1st H, ( $NaH_2PO_4$  (A) being formed); then, phenolphthalein (P) detns. the 2nd H ( $Na_2HPO_4$  (B) formed), and the 3rd is equiv. to that obtained in titrating back to M, or forward again to P. This also allows analysis of mixts. of HCl,  $H_3PO_4$  and A, or of A and B. A changing into B gives up  $\frac{1}{2}$  its H; but the analogous  $Fe^{++}$  and Ca salts, which are involved here chiefly, act differently. While neutral to M, they dissociate in titrating between M and P and give up  $\frac{2}{3}$  of their H, thus:  $3Ca(H_2PO_4)_2$ , i. e.,  $Ca_3(PO_4)_2 \cdot 4H_3PO_4$  on neutralizing does not form 3  $CaHPO_4$  and 3  $Na_2HPO_4$ , but yields the compd.  $Ca_3(PO_4)_2 \cdot 4Na_2HPO_4$ .  $Ca_3(PO_4)_2$  is pptd. and the filtrate contains 4  $Na_2HPO_4$ , i. e.,  $\frac{1}{3}$  of the acid H in the Ca or  $Fe^{++}$  salts, which may then be detd. by back titration. The procedure of the detn. and the calcn. of results are described in detail. In place of M, J. prefers the more sensitive  $Me_2NC_6H_4N:NC_6H_4$ , Toepfer's reagent for gastric HCl. S. WALDBOTT

**Note on calcium phosphate.** A. J. JONES. *Pharm. J.* 108, 62-3; *Chemist and Druggist* 96, 116-7(1922).—Calcii phosphas Brit. Pharm. is a mixt. of the tribasic and predominating dibasic salts ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ). By soln. in a definite amt. of standard HCl, and differential titration, with Toepfer's reagent and phenolphthalein as indicators (cf. preceding abstr.)  $\text{Ca}_3(\text{PO}_4)_2$  varied in 5 samples from 10.2 to 33.5%,  $\text{CaHPO}_4$  from 65.7 to 43.2%,  $\text{H}_2\text{O}$  from 16.0 to 20.8%. The chief impurity is sulfate; other impurities are  $\text{FePO}_4$  and  $\text{AlPO}_4$ , and Si compds.

S. WALDBOTT

**Oregon balsam.** E. M. HOLMES. *Pharm. J.* 108, 146-7(1922).—H. reviews the literature on the properties and botanical origin of this intended substitute for Canada balsam (cf. C. A. 7, 3530, 13, 1937). Accounts of the mode of collection of both balsams are quoted.

S. WALDBOTT

**An incompatible powder: calomel, phenalgin and acetylsalicylic acid.** J. NOBLE. *Pharm. J.* 108, 151; *Chemist and Druggist* 96, 235(1922).—When  $\text{HgCl}_2$  was added to the phenalgin, (P) especially when moist, it turned gray and dark. P was found to be a mixt. of  $\text{AcNHPh}$  60,  $\text{NaHCO}_3$  25,  $(\text{NH}_4)_2\text{CO}_3$  15%; the reaction was that of  $(\text{NH}_4)_2\text{CO}_3$  on  $\text{HgCl}_2$  (Ruddiman). Besides, in aq. soln., the 2 carbonates will be acted upon by the acid (A), more slowly in powder form. When P and A were first triturated together and  $\text{HgCl}_2$  was then added, no darkening took place. For P, tablets or capsules seem to be the only suitable method of dispensing.

S. WALDBOTT

**An incompatible ointment: iodine and mercuric nitrate.** JOHN NOBLE. *Pharm. J.* 108, 151-2; *Chemist and Druggist* 96, 235(1922).—An ointment was made of 2 drams each of Brit. Pharm. unguent. hydrarg. nitrat. dil. (A), ung. iodi (B) and paraffinum molle. Evidently, all of the  $\text{Hg}^{++}$  salt will be decomposed by the KI of B forming  $\text{HgI}_2 \cdot 2\text{KI}$ , and this, together with free I, replaces the action of  $\text{Hg}(\text{NO}_3)_2$ .

S. WALDBOTT

**Note on concentrated infusion of senega (1 to 7).** J. BREMNER. *Pharm. J.* 108, 152; *Chemist and Druggist* 96, 235(1922).—A sample, probably old, had an abundant, gelatinous ppt.; only 12% of the fluid could be filtered. No doubt enzymic action causing coagulation of pectinous substances also destroys the glucosidal saponins and renders the infusion unsightly and therapeutically inert. In discussion the addition of a small amt. of  $\text{NH}_4\text{OH}$  was suggested as a remedy against pptn.

S. WALDBOTT

**The advantages of the metrical system for prescribing.** W. C. SILLAR. *Pharm. J.* 108, 152-6; *Chemist and Druggist* 96, 236-7(1922).—An address, with discussion.

S. WALDBOTT

**The new Italian Pharmacopeia.** ANON. *Pharm. J.* 108, 240-2(1922).—A survey of its special features, e. g., sterilization, and translation of 4 typical monographs.

S. WALDBOTT

**Secale cornutum and so-called substitutes for ergot.** A. TSCHIRCH. *Schweiz. Apoth. Ztg.* 60, 1-6(1922).—Ergolamine,  $\text{C}_{23}\text{H}_{33}\text{N}_3\text{O}_5$  (Gynergen, Sandoz) of Stoll (*Verh. d. Schweiz. Naturf. Ges.* 1920, 19; *Helv. Chim. Acta* 1921; cf. C. A. 16, 464), is the carrier of the principal activity of ergot (cf. C. A. 11, 2531; 15, 923). It induces rhythmical contractions in the muscles of the uterus, even in dilns. of 1 : 20000000 (Spiro, *Schweiz. mediz. Wochschr.* 1921, Nos. 23, 32). The activity of exts. of ergot is due to intermediary bases, e. g., tyramine and histamine, resulting from the gradual demolition of the albumin mol.; yet the moment of max. activity due to max. amine content is uncertain. The occurrence of such bases in other plants (C. A. 14, 311, 448; 15, 2692) must be due to the same cause, but these are too uncertain to be proper substitutes for ergot; at times they are wholly inactive. Incidentally, T. describes the prepn. and spectroscopic properties of sclererylthrin and of a third coloring matter in *secale cornutum*, probably a deriv. of scleroxanthin. It is insol. in  $\text{H}_2\text{O}$ , sol. in concd.  $\text{H}_2\text{SO}_4$  with beautiful red, in  $\text{EtOH}$  with yellow color.

S. WALDBOTT

The cultivation of ergot. L. HÄCKER. *Schweiz. Apoth. Ztg.* 60, 45-51(1922); cf. C. A. 16, 1129.—Methods of production of sphacelia for the infection of flowering rye, and the procedure of mass infection are described in detail. S. WALDBOTT

Ferrum mangano-peptonatum solutum. HAUSER. *Schweiz. Apoth. Ztg.* 60, 71-2(1922).—When solns. of  $MnCl_2$  and peptone were mixed with old soln. of Fe oxychloride, an almost quant. pptn. of  $Fe(OH)_3$  took place. With a freshly prepd. Fe soln. (Pharm. Helv. IV), the mixt. remained clear, also when the Fe soln. was 2 months old. Probably colloidal changes take place later. S. WALDBOTT

Gelatina zinci. FLEISSIG. *Schweiz. Apoth. Ztg.* 60, 83(1922).—Mix  $ZnO$  1000.0, animal gelatin 2200.0, glycerol 3500.0, aqua borata (3.5 %) 3300.0. This Zn jelly, an improvement over that of Pharm. Helv. IV, keeps for a long time. S. W.

The drugs of Pegolotti. L. ROSENTHALER. *Schweiz. Apoth. Ztg.* 60, 89-96 (1922).—A review of the book *La pratica della mercatura* scritta da Francesco Balducci Pegolotti; Lisbon and Lucca, 1766 (Strassburg), printed from P's manuscript (Florence) of about 1335. S. WALDBOTT

Tinctura iodi. FLEISSIG. *Schweiz. Apoth. Ztg.* 60, 96-7(1922).—In the place of this unstable and dangerous prepn., F. proposes a soln. of I 50.0, KI 40.0, EtOH to make 1000 cc. The I content is less than that of Pharm. Helv., but the prepn. is sufficiently antiseptic, and HI is not liable to be set free. S. WALDBOTT

Solutio cocaini hydrochlorici. FLEISSIG. *Schweiz. Apoth. Ztg.* 60, 97(1922).—To avoid formation of molds which appear in even high % cocaine solns. F. dissolves the cocaine in aqua borata, when approved by the prescribing physician. S. WALDBOTT

The cultivation of medicinal plants, and experiments to increase their content of active principles. A. TSCHIRCH. *Schweiz. Apoth. Ztg.* 60, 129-6, 145-51(1922); cf. C. A. 11, 3377.—An historical and geographical review. With alkaloidal plants, hybridization and selective cultivation will be more effective in producing plants with higher alkaloidal yield than, e. g., expts. with fertilizers. The bibliography given supplements that of T.'s "Handbuch." S. WALDBOTT

Geneva apothecaries of the 15th to the 18th centuries. L. REUTTER. *Schweiz. Apoth. Ztg.* 60, 136-41(1922).—Illustrates the local pharmaceutical history of that period. S. WALDBOTT

Geneva public hygiene in past times. L. REUTTER. *Schweiz. Apoth. Ztg.* 60, 151-4, 162-6, 173-6, 189-94(1922).—Chiefly an account of the treatment of leprosy and the plague at Geneva during the 15th and 16th centuries. S. WALDBOTT

The alkaloidal assay method of Pharmacopœia Helvetica IV, for aconite root, and its improvement. C. E. BRUNNER. *Schweiz. Apoth. Ztg.* 60, 169-73, 185-9, 197-202, 209-15(1922).—The Pharm. Helv. method of extrn. of this root is very satisfactory; to expel  $NH_3$ , simply distg. off the  $Et_2O$  is not sufficient. Distil the residue repeatedly with neutral  $Et_2O$  until the distillate no longer reddens a neutral  $Et_2O-H_2O$  mixt. contg. iodoeosin (A). In place of abs. EtOH, dissolve the  $NH_3$ -free distn. residue directly in 25 cc. of neutral  $Et_2O$  contg. A, and add before titration 10 cc.  $H_2O$  neutral to A. Replace hematoxylin by A. A modified method of dctn. is based on these results. In parallel dctns. made on the same material, the max. deviations by this method were 4.1%-0.9% of the % of alkaloids found; by the official method, the deviations were 7.9%. S. WALDBOTT

Notes on perfumery. L. REUTTER. *Schweiz. Apoth. Ztg.* 60, 215-7(1922).—A general survey of the materials entering into perfumery, and their mode of combination. S. WALDBOTT

The hydrocyanic acid question. XI. The hydrocyanic acid glucoside of *Dimorpha theca ecklonis* D. C. L. ROSENTHALER. *Schweiz. Apoth. Ztg.* 60, 234-6(1922); cf.

*C. A.* 16, 1107.—This S. African composite is poisonous to cattle; Greshoff (*C. A.* 1, 1165, 3, 1893) has shown that it contains HCN. On distn. of authentic material (A. Theiler, *Mitteil. d. naturf. Ges. Bern* 1921, Heft III) R. obtained from leaves 1.247%, green stems 0.374, older brown stems 0.143, flower heads 0.826% HCN; besides,  $\text{Me}_2\text{CO}$  distd. By extg. the leaves with EtOH, purifying with  $\text{Pb}(\text{OAc})_2$  and recrystg. from AcOEt, a white, silky glucoside, m.  $144^\circ$ ,  $[\alpha]_D -28.65^\circ$ , was obtained. Upon hydrolysis, dextrose and equiv. amts. of HCN and  $\text{Me}_2\text{CO}$  were formed, and the glucoside proved to be identical with *linamarin*,  $\text{NCCMe}_2\text{C}_6\text{H}_9\text{O}_6$ . HCN is not present in the plant in the free state.

S. WALDBOTT

The juniper berry and some of its preparations. J. PRITZKER AND R. JUNGKUNZ. *Schweiz. Apoth. Ztg.* 60, 245-9, 257-61, 270-5(1922).—Data are supplied for the analysis of the berry and its preps., some of which are secret nostrums. The av. compn. of the juniper berry is: Dry substance 90.90%; thereof  $\text{H}_2\text{O}$ -sol. 45.35%; N substances 3.05; essential oil 2.61; fat 9.5; invert sugar 32.8 (König 20.61%); pentosans 6.82; other N-free ext. 17.46; crude fiber 16.0 (König, 20.55%); ash 2.64%; alkali no. 13.87 (cc. N acid to neutralize 1 g. mineral matter); sucrose: absent; this fact permits detection of added cane sugar. Standard juniper berry juices, sirups, wine and brandy were then prepd. and analytical data obtained and discussed. The consts. and other phys. and chem. properties of the fat and the essential oil are tabulated. Oleum juniperi, but not the fat, gives the Storch-Morawski test distinctly.

S. W.

CAUSSIN: Les plantes médicinales de la Picardie. Paris: Vigot frères, 23, place de l'Ecole de Médecine. 5 fr. Reviewed in *J. pharm. Belg.* 4, 87(1922).

GORIS, A. and DEMILLY, J.: La culture des plantes médicinales. Paris: Vigot frères. 4 fr. Reviewed in *J. pharm. Belg.* 3, 856(1921).

SCHMIDT, ERNST: Ausführliches Lehrbuch der pharmazeutischen Chemie. Zweiter Band: Organische Chemie. Erste Abteilung: Organische Verbindungen mit offener Kohlenstoffkette. 6th Ed., revized. Braunschweig: Friedr. Vieweg & Sohn. 1082 pp. f 21., bound f 25.50. Reviewed in *Chem. Weekblad* 19, 243(1922); *Z. angew. Chem.* 35, 192(1922).

Antiseptics and preservatives. M. MAS. Brit. 176,339, Feb. 9, 1922. An antiseptic and preservative prepn. comprizes a salt of Zn to which phenol or an alk. salt thereof has been added. The ingredients may be mixed in the cryst. state or in soln. In an example phenol is added to  $\text{ZnCl}_2$  when the latter is at its m. p. It is stated that the addn. of phenol permits the use of a smaller proportion of coal-tar creosote than that usually added to Zn salts used as preservatives.

Mouth wash. E. LONDON. U. S. 1,416,666, May 16.  $\text{KClO}_4$ , 10, fl. ext. of *Hamamelis virginiana* 65-100 and alc. 25 pts.

Dentifrices. W. S. ROGERS. Brit. 176,271, May 3, 1921. A dentifrice comprizes a mixt. of S and an alk. substance. The mixt. may consist of 80 pts. of washed flowers of S and 20 pts. of  $\text{NaBO}_3$  to which a small quantity of oil of gaultheria may be added.

Albumins from blood. A. J. L. TERWEN and C. J. C. VAN HOOGENHUYZE. U. S. 1,415,277, May 9. See Brit. 123,971 (*C. A.* 13, 1621).

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

The distillation of aqueous nitric acid and nitric acid-sulfuric acid mixtures. E. BGRL AND O. SAMYLEBEN. *Z. angew. Chem.* 35, 201-2, 206-11(1922).—This is

practically a repetition of the work of Pascal and Garnier (cf. *C. A.* 15, 3183), but with mixts. more nearly free from N oxides, and only at atm. pressure. The exptl. app. used was nearly the same as before, but the method was different and probably more accurate. The results differ somewhat from those of Pascal and Garnier, but are too numerous to be abstracted. They are given in the form of graphs showing the relation between boiling aq.  $\text{HNO}_3$  solns. and their vapors, boiling  $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-H}_2\text{O}$  mixts. and their vapors and the b.p.'s of  $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-H}_2\text{O}$  mixts. The use of triangular coordinates in graphic calcns. is discussed. F. C. Z.

Atmospheric pollution from sulfuric acid plant fumes. J. R. WITHROW. *Chem. Met. Eng.* 26, 972-6, 1106(1922).—The importance of the fume problem to the chem. mfr. is discussed from the standpoint of public health, legislation and better operation, and the work of the Atmospheric Pollution Committee of the Amer. Inst. Chem. Eng. is reviewed. F. C. Z.

The U. S. Government explosives plant C, Nitro, West Virginia. II. The manufacture of sulfuric acid by the contact process. MARCH F. CHASE AND F. E. PIERCE. *J. Ind. Eng. Chem.* 14, 498-503(1922); cf. *C. A.* 16, 1867.—The design of the plant is described in considerable detail. Schroeder-Grillo mass was used. An alignment chart for calc. conversion is shown. F. C. Z.

Production of ammonia by the sodium cyanide method. F. F. BARTELL. *J. Ind. Eng. Chem.* 14, 516-21(1922).—Expts. on hydrolyzing NaCN were carried out at 1 atm. and various temps. with varying amts. of steam. Recoveries as high as 99-100% were obtained in batch retorts. A continuous hydrolyzer was developed which in one trial run gave a 97.8% recovery. F. C. Z.

The future of nitrogen fixation in the United States. J. K. CLEMENT. *Chem. Age* (N. Y.) 30, 197-8(1922). E. J. C.

Can we afford to make potash in America? R. N. SHREVE. *J. Ind. Eng. Chem.* 14, 542-4(1922).—The manuf. of potash in America should show a large saving, with comparatively moderate increase in price to the farmer. F. C. Z.

The manufacture of barium chloride. STEINAU. Nurnberg. *Chem.-Ztg.* 46, 400-1(1922).— $\text{BaCl}_2$  is prepd. by heating barytes with coal and  $\text{CaCl}_2$  after preliminary drying. The fused mass is lixiviated. The pure salt is obtained by filtration and crystn. O. A. CHERRY

Preparation of sodium cyanide from calcium cyanamide. CHUJI FUJIOKA. *J. Chem. Ind. (Japan)* 24, 1119-30(1921).— $\text{Ca}(\text{CN})_2$  5,  $\text{Na}_2\text{CO}_3$  3,  $\text{NaCl}$  6, C 1, and powdered Zn, Al or Mg 2.5 parts are thoroughly mixd., heated in a closed vessel at 900-1000° for 10-20 min. and then cooled rapidly. With Zn, 80% of the N is utilized, yielding 14% NaCN; with Al, 85% of the N is utilized and 15% crude cyanide is obtained. With Mg, the reaction is nearly quant., yielding 17% NaCN. A mixt. of  $\text{CaCN}_2$  5,  $\text{NaCl}$  12, C 1, and Mg 2.5, shows equal efficiency in utilizing N, but the yield is about 14%. The comparatively high cost of these metals is the only disadvantage of this method. S. T.

Graphitic nature of the carbon of lime-nitrogen. NAOTO KAMEYAMA. *J. Chem. Ind. (Japan)* 24, 1131-42(1921).—Frank obtained graphite from  $\text{CaC}_2$  by heating with various gases (*C. A.* 6, 135), and N is mentioned among these gases. K. sepd. C from lime-nitrogen by means of HCl, and HF and examd. its nature. Its d., 2.246 (the sample had 0.67% ash) was the same as that of Acheson graphite (0.7% ash). Heat of combustion was 7857 g. cal. X-ray examn. (Debye-Scherrer), showed diffraction rings. Its elec. cond. was practically equal to that of Acheson graphite. When oxidized by Standenmaier's method, it gave graphitic acids. Since an enormous quantity of N is fixed by the cyanamide process, a large amt. of graphite must be available in



lime-nitrogen. If it can be economically sepd. it will be of industrial importance.

S. T.

Chromite in 1921. EDWARD SAMPSON. U. S. Geol. Survey, *Mineral Resources of U. S., 1921*, Pt. I, 15-17 (Preprint No. 3, publ. May 15, 1922).

E. J. C.

Fluorite in Mexico. E. WITTICH. *Bol. minero* (Mexico) 1921, 6 pp.—Occurrences are numerous, but the only production at present comes from the Sierra del Realajo, San Luis Potosi, in an immense contact zone.

M. R. S.

Oxygen production by the Claude process. ANON. *Chem. Age* (N. Y.) 30, 215-6 (1922).—A general description.

E. J. C.

Production of hydrogen by the use of ferro-silicon and sodium hydroxide. R. R. WEAVER. *Trans. Am. Electrochem. Soc.* 41, preprint (1922); cf. Report No. 40, in the 4th Annual report of the National Advisory Committee for Aeronautics.—The chief reaction in the "Silical" process for the production of H is regarded as taking place between Si and H<sub>2</sub>O with NaOH as a catalyst. Accordingly the relative amts. of alkali and ferro-Si to be used in practice should be detd. by the speed of reaction and the relative cost of the materials, rather than by computing the proportions corresponding to a definite equation. The plant required consists of a soln. tank, a generator, and a washer. A ferro-Si contg. 0.90 Si gives nearly theoretical quantities of H; one contg. less than 0.75 Si is almost useless for this purpose. Temp. control of the process is important and the temp. should not be allowed to rise too high. The ratio of NaOH to Si should not be greater than 1 : 1 by wt. The ferro-Si method is especially adapted to military and naval use because of the relatively small size and low cost of the generator required to produce H at a rapid rate, the small operating force required, and the fact that no power is used except the small amt. required to operate the stirring and pumping machinery.

D. MACRAE

The manufacture of reflecting surfaces. K. GUNDLACH. *Naturwissenschaften* 10, 117-9(1922).—A discussion of a recent symposium ("A Discussion of the Making of Reflecting Surfaces held on Nov. 26, 1920 at the Imperial College of Science and Technology, So. Kensington," Fleetway Press, Holborn). The subjects are treated historically, scientifically and technically and include (1) a survey of the bibliography on metallic deposition on glass; (2) a bibliography of the important papers on the construction and nature of reflecting surfaces; (3) the formaldehyde process of silvering; (4) workshop notes on silvering; (5) silvering of glass reflectors by chem. deposition; (6) silvering of a large reflector; (7) silvering of quartz and glass fibers; (8) mirrors used for reflecting heat radiation; (9) deposition of metals by cathodic sputtering *in vacuo*; (10) production of mirrors by cathodic bombardment; (11) Pt reflecting surfaces prepd. by the burning-in process; (12) mirrors for use in optical instruments under industrial conditions and (13) a photometric method of measuring the reflecting power of mirrors.

C. C. DAVIS

Failure of cast and high-silicon iron in fuming sulfuric acid (BANIGAN) 9. Modern preparation of aqueous ammonia (ILLERT) 1.

LEHNER, SIGMUND: *Kitte und Klebemittel*. 9th Ed. revized by Friedrich Wächter. Vienna: A. Hartleben. M 20.

Arsenic acid. C. ELLIS and V. T. STEWART. U. S. 1,415,323, May 9. A mixt. of As<sub>2</sub>O<sub>3</sub> with a slightly less amt. of H<sub>2</sub>O is reacted upon with gaseous Cl and after the formation of a soln. the supply of Cl is continued to produce arsenic acid by oxidation.

Sulfuric acid. G. F. HURT. U. S. 1,415,353, May 9. Cases from the Glover

tower are passed through a chamber and thence back into an intermediate part of the Glover tower for recirculation; this increases the output and uniformity of the  $\text{H}_2\text{SO}_4$  produced.

**Manganese dioxide and nitric acid.** C. J. REED. U. S. 1,415,395, May 9. A mixt. of aq. Mn sulfate is heated with  $\text{NaNO}_3$  or other nitrate to volatilize  $\text{HNO}_3$  and leave a residue which contains  $\text{MnO}_2$  adapted for recovery by washing and drying.

**Caustic alkalies.** C. DEGUIDE. Brit. 176,321, Dec. 20, 1921. The decompn. of Ba silicates with  $\text{H}_2\text{O}$  and an alkali sulfate as described in 174,581 (C. A. 16, 1838) is effected with suitable proportion of alkali sulfate so as to obtain caustic alkalies and a residue of mono-barium silicate and  $\text{BaSO}_4$ , which on calcination with C yields again the original Ba silicate, *i. e.*, either  $\text{SiO}_2 \cdot 2\text{BaO}$  or  $\text{SiO}_2 \cdot 3\text{BaO}$  or an intermediate silicate. One mol. of sulfate is used to one mol. of the di-barium silicate, and 2 mol. of sulfate to 1 mol. of the tri-barium silicate.

**Decolorizing caustic alkali.** T. C. MEADOWS and H. D. RUHM. U. S. 1,415,186, May 9. Conc'd. caustic alkali is bleached by passing an elec. current through it.

**Synthetic ammonia.** SOC. L'AIR LIQUIDE (SOC. ANON. POUR L'ETUDE ET L'EXPLOITATION DES PROCÉDÉS G. CLAUDE). Brit. 174,041, Nov. 10, 1921. To facilitate the renewal of the catalytic material employed for the synthesis of  $\text{NH}_3$ , the inner tube contg. the catalyst is rigidly secured to the removable head of the permanently fixed outer pressure tube. Cf. 171,970 (C. A. 16, 1134) and 171,972 (C. A. 16, 1134). A suitable construction is specified.

**Ammonia; sodium bicarbonate.** E. W. PATTISON. Brit. 176,400, Sept. 3, 1920. In a modified ammonia-soda process,  $\text{NH}_3$  is liberated from the  $\text{NH}_4\text{Cl}$  by treating with an alk. earth sulfide and converting the resulting  $(\text{NH}_4)_2\text{S}$  into  $\text{NH}_3$  by means of an alkali. In the preferred method of working, feeder liquor from the bicarbonate filters after passing through a heater whereby the  $\text{NH}_4\text{HCO}_3$  present is decomposed, passes to the distg. section through a pipe, whereupon  $(\text{NH}_4)_2\text{S}$  and  $\text{BaCl}_2$  are produced by interaction with  $\text{BaS}$  obtained by lixiviation of black-ash and introduced through a pipe. The  $(\text{NH}_4)_2\text{S}$  passes to the receptacle and is treated with  $\text{NaOH}$  to give  $\text{Na}_2\text{S}$  and free  $\text{NH}_3$ , which is conveyed to the absorbers.  $\text{Na}_2\text{CO}_3$  may be employed in place of  $\text{NaOH}$  but slight excess is required, which contaminates the  $\text{Na}_2\text{S}$ , and also  $\text{NH}_4\text{HCO}_3$  instead of  $\text{NH}_3$  is produced. The  $\text{Na}_2\text{S}$  liquor is removed through another pipe and is treated either with a little  $\text{HCl}$  to convert the small quantity of  $\text{BaS}$  present into  $\text{BaCl}_2$  or is treated with  $\text{CO}_2$  to ppt. the sulfide as carbonate. The  $\text{BaCl}_2$  is sepd. from the  $\text{NaCl}$  present by fractional crystn. Alternatively, the  $\text{NH}_4\text{Cl}$  is crystd. from the feeder liquor, and its soln. in  $\text{H}_2\text{O}$  treated with alk.-earth sulfide.

**Hyposulfites.** FARBENFABRIKEN VORM. F. BAYER & CO. Brit. 176,344, Feb. 20, 1922. Hyposulfites are produced by reducing bisulfites by means of an amalgam such as Na amalgam in the presence of an acid such as  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_3$  or  $\text{HCl}$ . The quantity of acid added is preferably equiv. to the metal dissolved in the Hg. The amalgam may be produced electrolytically and led by a siphon to a closed vessel contg. the bisulfite soln., the Hg being returned to the electrolytic cell.

**Barium chloride.** MATHIESON ALKALI WORKS, INC. Brit. 157,879, Oct. 22, 1920.  $\text{BaCl}_2$  is prepd. from  $\text{BaS}$  obtained by reducing barytes with coal dust by treatment with  $\text{NH}_4\text{Cl}$ . The latter may advantageously be obtained from the "feeder liquor" resulting from the Solvay process. In a still, supplied with "feeder liquor" at the top, the  $\text{NH}_4\text{HCO}_3$  is driven off by the exhaust steam led in at the bottom, and the remaining soln. contg.  $\text{NH}_4\text{Cl}$  and  $\text{NaCl}$  is passed to an evaporator.  $\text{NaCl}$  is deposited in the latter and is removed while the residual  $\text{NH}_4\text{Cl}$  soln. is purified by recrystn. and conveyed to a second still. Clear  $\text{BaS}$  soln. obtained by lixiviation of black ash, is also conveyed to this second still. The resulting liquor is freed from  $(\text{NH}_4)_2\text{S}$  by the passage of exhaust

steam and evapd. until  $\text{BaCl}_2$  crystallizes out.  $\text{NH}_3$  may be recovered from the  $(\text{NH}_4)_2\text{S}$  evolved from the still by absorbing the vapors in  $\text{NaOH}$  and passing steam. The  $\text{NH}_3$  is utilized in the Solvay process. Alternatively the  $\text{BaS}$  may be mixed with the "feeder liquor" before the  $\text{NaCl}$  is sepd., and the  $\text{NaCl}$  sepd. from the  $\text{BaCl}_2$  at a subsequent stage.

**Antimony sulfide.** A. L. STARK. U. S. 1,415,127, May 9. Finely ground stibnite is mixed with  $\text{S}$ ,  $\text{Ba}$  sulfide,  $\text{H}_2\text{O}$  and  $\text{NaOH}$  and the mixt. is heated under pressure to form a  $\text{H}_2\text{O}$ -sol. salt of  $\text{Sb}$  and  $\text{Ba}$ .  $\text{H}_2\text{SO}_4$  is then added to ppt.  $\text{Sb}_2\text{S}_3$  and  $\text{BaSO}_4$ . The pptd. mixt. is made up of  $\text{BaSO}_4$  particles coated with  $\text{Sb}_2\text{S}_3$ .

**Separating salts from brines.** E. P. STEVENSON. U. S. 1,415,206, May 9. Alk. brine contg.  $\text{Na}_2\text{CO}_3$  is treated with  $\text{CO}_2$  to ppt.  $\text{NaHCO}_3$ . The ppt. is decomposed with  $\text{CaSO}_4$  to obtain  $\text{Na}_2\text{CO}_3$  and  $\text{CO}_2$  and additional  $\text{CO}_2$  is obtained by treating the filtrate from the  $\text{NaHCO}_3$  with  $\text{CaSO}_4$ . The  $\text{CO}_2$  thus regenerated is used for treating additional brine.

**Borax from brines.** E. P. STEVENSON. U. S. 1,415,205, May 9. Brine such as that from Searles Lake is chilled to below  $0^\circ$  to ppt. borax together with some other salts such as small amts. of  $\text{NaCl}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$  and these latter are then separated from the pptd. mixt. by washing with satd.  $\text{NaCl}$  to dissolve borax, which is then recrystd.

**Potash from brine.** E. P. STEVENSON. U. S. 1,415,203, May 9. Searles Lake brine or similar brine is chilled to ppt. a large part of the salts except  $\text{NaCl}$  and  $\text{KCl}$  and these two chlorides are then sepd. by evapn. to dryness and extn. with satd.  $\text{NaCl}$  soln. U. S. 1,415,204 specifies chilling the brine to ppt. comparatively worthless salts, evapg. to dryness, treating the dried salts with  $\text{CaSO}_4$  or other pptg. agent for waste salts and then extg.  $\text{K}$  values.

**Recovery of potash from cement mixtures.** D. D. JACKSON. U. S. 1,415,572, May 9. Cement mixts. contg. insol.  $\text{K}$  compds. are heated in a kiln to a temp. sufficient to form cement while  $\text{H}_2\text{O}$  vapor is introduced to promote formation and volatilization of  $\text{KOH}$ .

**Potassium alum from slate.** C. R. HAYWARD and H. M. SCHLEICHER. U. S. 1,415,346, May 9.  $\text{K}$ -bearing slate is heated with  $\text{H}_2\text{SO}_4$  sol. sulfates are leached out and  $\text{K}$  alum is crystd.

**Decomposing aluminium sulfate.** H. M. BURKEY and H. M. SCHLEICHER. U. S. 1,415,308, May 9. A soln. of  $\text{Al}_2(\text{SO}_4)_3$  or alum is heated under pressure to obtain  $\text{H}_2\text{SO}_4$  and basic compds.

**Titanium sulfate and oxide.** CHEMISCHE WERKE VORM. AUERGES (formerly Ges. für Verwertung Chemischer Produkte). Brit. 173,774, Jan. 5, 1922. A crude soln. of sulfates obtained from titaniferous  $\text{Fe}$  ore is treated for the removal of the  $\text{Fe}$  by first reducing and then sepg. the  $\text{FeSO}_4$  by crystn. Preferably the soln. is reduced by metallic iron.  $\text{TiO}_2$  free from  $\text{Fe}$  is obtained by hydrolysis of the purified  $\text{Ti}$  sulfate soln.

**Zinc oxide.** A. PEARSON. Brit. 176,588, Jan. 17, 1921. Crude  $\text{ZnO}$  contg. colored oxides of  $\text{Cd}$  and  $\text{Pb}$  is mixed with a small quantity of  $\text{ZnSO}_4$  or  $\text{H}_2\text{SO}_4$  and calcined in a muffle at a temp. not exceeding  $878^\circ$ , preferably  $720$ – $820^\circ$ , so as to convert the  $\text{Cd}$  and  $\text{Pb}$  into white compds. The  $\text{ZnSO}_4$  added should be finely divided.

**Silicon nitrogen compounds.** F. VON BICHOWSKY. U. S. 1,415,280, May 9. A charge contg.  $\text{Ti}$ -bearing sand,  $\text{Fe}$ ,  $\text{Ni}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}$  silicate is heated to a temp. of about  $1100$ – $1300^\circ$  with  $\text{CH}_4$  and  $\text{N}$  but in the absence of free  $\text{C}$ , to produce  $\text{SiN}$  compds for fertilizers or for producing  $\text{NH}_3$  or  $\text{CN}$  compds.

**Sulfur.** J. Y. JOHNSON. Brit. 174,143, Oct. 12, 1920.  $\text{S}$  is extd. from charcoal which has been employed as a contact mass for removing  $\text{H}_2\text{S}$  from gases by oxidation with air, by means of  $(\text{NH}_4)_2\text{S}$  soln. The soln. is boiled in a still, the vapors pass to a con-

denser and the condensed  $(\text{NH}_4)_2\text{S}$  runs through the vessel, which contains the spent charcoal; the soln., satd. with S, flows back to the still, in which S accumulates. On continuing the distn. the condensate eventually becomes practically free from  $(\text{NH}_4)_2\text{S}$  and serves for finally washing the charcoal, after which it is diverted into a receiver. The pptn. of the S in the still may be facilitated by adding an electrolyte, *e. g.*, salt. The parts of the app. which are exposed to the  $(\text{NH}_4)_2\text{S}$  soln. are preferably made of or coated with Al or its alloys. Cf. 13,383, 1911(C. A. 6, 3500) and 1415, 1914. The provisional specification refers to the extn. of S from exhausted gas-purification masses in general. A suitable construction is specified.

**Iodine.** O. VON FABER. Holl. 6779. Apr. 15, 1922. I which has been adsorbed in C is obtained by burning the C either with the aid of air or O in a combined form. The heat produced is used for other purposes. Cf. C. A. 16, 319.

**Activated carbon.** GENERAL ELECTRIC CO. Brit. 176,476, Dec. 2, 1920. Carbonaceous materials are distd. for about 8 hr. in refractory retorts at about 700–1000° and steam or other oxidizing-gas is admitted after at least 2 hr. The product may be used for the following purposes, namely, the production of high vacua and removal of the last traces of gas from incandescent lamps, etc.; the removal of arsine from H and hydrocarbon vapors from air and natural and artificial gases; the recovery of solvents, *e. g.*, the absorption of gasoline from an admixt. with air, obtained by distg. off excess solvent from rubber soln.; the removal of gasoline from natural gas; the clarification of liquids and purification of  $\text{H}_2\text{O}$ ; the administration of anesthetics; as an absorbent for use in gas masks; or as a catalyst.

**Treating fruit kernels.** H. R. and L. E. SCOTT. U. S. 1,416,128, May 16. Kernels of prunes, peaches or apricots are treated with  $\text{H}_2\text{O}$  to decompose amygdalin by the emulsin present, BzH and HCN products are removed by filtration and the filtrate is distd. separately to recover these products. The kernel residue is washed to recover additional sol. products.

**Cellular alginate composition.** B. F. ERDAHL. U. S. 1,415,850, May 9. A cellular or pervious material such as *paper pulp* is provided with a filling or film of colloidal alginate-gel to render it cohesive and impermeable.

**Gelling metal alginates.** B. F. ERDAHL. U. S. 1,415,849, May 9. A metal compd. such as  $\text{FeCl}_3$  in cold aq. soln. is treated with Na alginate, impurities present are eliminated by washing and a substance such as cold  $\text{NH}_3$  soln. is added to transform the reaction product into a colloidal alginate-metal gel. All the reactions are carried out without heating.

**Catgut.** S. UYAMA. Brit. 176,679, March 19, 1921. Catgut is prepd. by a process that allows the intestines of large animals, such as cows, horses, donkeys, mules, etc., to be used. An intestinal tube, preferably a jejunum, is ligatured at each end. Near one ligature, the external layer, that is the serous membrane and outer longitudinal muscle layer, is incized circumferentially and stripped off in one film. This film is treated with an alkali, such as NaOH or potash, till it expands and becomes translucent, and then foreign materials are shaved off and the film is washed in  $\text{H}_2\text{O}$ . The film is cut into strips, rolled into yarn, and dried under increasing tension. The catgut may be sterilized by dry heat for an hr. at a temp. of 160° or treated before rolling with a disinfectant such as I dissolved in KI, which is cleared by treatment with  $\text{Na}_2\text{S}_2\text{O}_4$ , and then sterilized by dry heat for a shorter period.

**Bleaching-earths.** SCHWEIZERISCHE SODAFABRIK. Brit. 176,353, Feb. 25, 1922. The activity of bleaching-earths comprizing Al hydrosilicates, *e. g.*, fullers earth, floridin, and Florida earth is increased by treating them in the cold with dil. acid, *e. g.*, HCl or  $\text{H}_2\text{SO}_4$  of 1% strength. The earth is afterwards filtered, washed with  $\text{H}_2\text{O}$ , and dried. Known processes, comprizing cautious heating to expel hygroscopic  $\text{H}_2\text{O}$ , or boiling for

2 hr. with HCl or  $H_2SO_4$  of 15% strength to produce for example "Tonsil" or "franconite," are referred to.

**Detergent.** W. C. NEWBURY. U. S. 1,415,605, May 9. A mixt. of creosote with light petroleum and linseed oils is used for removing tar or road oil from automobiles.

**Detergent powder.** J. W. SMITH. U. S. 1,416,240, May 16. A mixt. of  $NaHSO_4$  and powdered wood.

**Cleaning articles of gold, silver or platinum.** W. W. EVERTS. U. S. 1,416,403, May 16. The articles are immersed in a soln. of salt contg. a plate formed of Zn and Cu alloy.

**Metal polishes.** G. R. DALE. Brit. 176,531, Dec. 13, 1920. A liquid metal polish consists of a suspension of lampblack in distd.  $H_2O$  or other non-poisonous liquid, say 4 oz. in 1 pt. Scents and other gelatinous or other agents promoting suspension may be added. Cf. 1839, 1874, 24644, 1898 and 25,092, 1904.

**Composition for coating wood, metal, cloth or glass.** M. J. WALSH. U. S. 1,415,282, May 9.  $H_2SO_4$  5 oz., whiting 12 oz., gum rosin 5 oz., petrolatum 5 oz., mineral oil 1.25 pints, Na silicate 1.25 pints and kerosene 3 qts. are mixed, with small amts. of volatile oils as perfumes.

**Preventing condensation on windows, etc.** A. M. L. LACQUE. Brit. 173,770, Jan. 4, 1922. Condensation of  $H_2O$ , etc., is prevented on windows and particularly on wind-shields by rubbing the glass with a felt pad impregnated according to the following method: A homogeneous soln. is made of 5 g. of soap contg. olein, 5 g. of  $Na_2CO_3$  and 50 g. of  $H_2O$ . Three g. of this soln. are mixed with 1000 g. of  $H_2O$  and the felt is immersed therein for 24 hr. The felt is then air-dried and boiled for  $\frac{3}{4}$  of an hr. at low heat, in a closed vessel, contg. a mixt. of 10 g. glycerol, 10 g. alc., of 90° proof, 10 g.  $Na_2CO_3$ , 10 g. of  $NH_3$ , 2.5 g. of pure gelatin, 2.5 g. of colophane, 100 g. of  $H_2O$ . The colophane is first powdered and passed through a sieve, etc. The felts are well stirred during boiling and finally air-dried and can then be mounted in a holder. A suitable construction is specified.

**Coherent blocks for making aluminium nitride.** W. HOOPES. U. S. 1,415,036, May 9. Coherent and self-sustaining but porous blocks adapted for producing Al nitride with N are formed of bauxite, coke and tar by compressing, molding and baking.

**Shoe dressing.** P. THORNSON. U. S. 1,415,208, May 9. A mixt. of beef tallow, pine tar, rubber and neatsfoot oil.

**Lithopone.** CORDES & Co. GEs. Brit. 176,377, March 3, 1922. In making light-proof lithopone, the Zn salt soln., the baryta lye, and the  $H_2O$  used in the process are purified and clarified by producing small quantities of a purifying medium in the liquids. E. g., a small quantity of an Fe or Al salt is added, and pptn. is effected by adding a slight excess of a carbonate, phosphate or hydrate, the liquids being then boiled and filtered. The BaS soln. is obtained by treatment of a baryta lye, purified as described above, with  $H_2S$ .

**Plastic compositions.** H. FROOD. Brit. 176,404, Sept. 7, 1920. A compn. to be formed into sheets for the manuf. of boot soles and heels, disks for universal joints, etc., comprizes unwoven org. or inorg. fibers, or both, which have previously been treated with a cementitious substance such as the enamel described in 4627, 1909, a phenol-aldehyde condensation product or the like, incorporated with rubber or the like. The finished material may be made solid of the required thickness with or without reinforcements or it may be built up of two or more layers with or without intervening layers of wire, cord, or other reinforcement. Waste fabric, etc., which has been bonded with a cementitious substance may be disintegrated, or raw fibers may be specially treated with the enamel or the like. A suitable compn. is rubber 26, disintegrated previously treated

fibers 6, S 6, C black 1, and  $\text{CaO } \frac{1}{2}$ , vulcanized for  $1\frac{1}{2}$  hrs. at a steam pressure of 45 lb. per sq. in.

**Plastic compositions.** H. FROOD. Brit. 176,405, Sept. 7, 1920. A compn. for making floor coverings, etc., comprizes fibers which have been treated with a cementitious substance such as the enamel described in 4627, 1909, a phenolaldehyde condensation product or the like, and a binding agent such as rubber, casein, glue, etc. Fabrics which have been bonded with a varnish, enamel, etc., are disintegrated, or untreated fibers may be treated with a cementitious substance and stoved, the fibers being kept in a loose condition, or subsequently shredded again. The fibers may be fireproofed by treatment with Na silicate,  $\text{ZnCl}_2$ ,  $\text{SbCl}_3$ , etc. The binding agent may also be fireproofed by known means. Designs may be formed by removing portions and filling the holes with compn. of a different color. Other fillers may be added, and the sheet may be reinforced. A suitable compn. consists of rubber 40,  $\text{MgO}$  1, S 2, disintegrated cotton fibers previously treated with cementitious substance 5, vulcanizing accelerator  $\frac{1}{4}$ , wood meal  $15\frac{1}{4}$ , ultramarine 2,  $\text{ZnO}$  19, and kieselguhr 15 pts., which is sheeted and vulcanized in 1 hr. at a steam pressure of 45 lb. per sq. in.

**Artificial gems.** F. SAUVAGE. Brit. 176,687, Apr. 4, 1921. Artificial pearls, half pearls, paste diamonds, and imitation rubies, emeralds, opals, etc., are caused to exhibit a change in color when viewed in twilight and to be luminous in the dark, by coating the interior or back with a phosphorescent substance; the use of radio-active  $\text{ZnS}$  imparts an emerald green color in the twilight. As applied to artificial pearls which should be thin-walled or transparent, or obtained from an orient such as ablet scales, essence of orient, crystal powder, the phosphorescent material may be mixed therewith. If necessary, a protective varnish may be first applied to the orient of the pearl, and may also be applied to the phosphorescent material, or the latter may be applied to the hollow core of a pearl which may be then filled up with wax. Imitation gems so produced may be set in jewelry or used in signs, arrows, letters, designs, etc.

**Bottle capsules, etc.** A. A. DILITZ. Brit. 176,367, March 1, 1922. Caps for sealing covers of vessels consist of a dry pellicle of acetylcellulose and water-soluble softening material, such as acetin, the caps being immersed in  $\text{H}_2\text{O}$  after being applied to the vessels to be sealed, with the result that they shrink and adhere strongly after drying. As an example, 10 pts. of acetin are added to 10 pts. of acetylcellulose dissolved in 90 pts. of acetone, and a film of the desired thickness is formed on a glass mold inserted in the soln. The film is stripped off and may be sprinkled with talc and rolled up. Filling and coloring materials, such as bronze powder, may be added to the soln.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**Effect of the rays from radium, X-rays, and ultraviolet rays on glass.** J. R. CLARKE. *J. Soc. Glass Technology* 5, 155-65(1921).—A series of soda-lime glasses of the same compn., except that some contained Se, some Co oxide, and others no admixture, has been exposed to the action of  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays,  $\beta$ - and  $\gamma$ -rays,  $\gamma$ -rays, X-rays, and ultraviolet rays, resp. All glasses contg. Se or Co oxide were colored brown by  $\beta$ -rays, the depth of coloration corresponding with the range of the  $\beta$ -particles in the glasses. The intensity of coloration was greatest at the surface, decreased toward the interior, and increased with increasing Se or Co oxide content. As the radiation was prolonged, the intensity increased to a max., which depended on the percentage of coloring agent, and then remained const. The pure soda-lime glass was only affected by  $\alpha$ -rays, being faintly colored on the surface only. None of the glasses was affected by X-rays,  $\gamma$ -rays, or

ultraviolet rays. All the glasses fluoresced in Ra Em, but a fatigue effect was observed at about the same time as the attainment of max. intensity of coloration. The coloration of glasses is regarded as due to the formation of colloidal particles in the glass. The presence of such particles is explained as being due to the action of  $\alpha$ - or  $\beta$ -rays on ions already present in the glasses. The fluorescence is held to be due to mechanical bombardment of the glass mols. by the rays. J. C. S.

The new corundum industry in the northern Transvaal (HALL) 8.

DORNGES, WILLY: *Meissner Porzellan*. 2nd Ed. Dresden: Wolfgang Jess. 236 pp. M 75, bound M 95. Reviewed in *Tonind. Z.* 45, 1257(1921).

Jahr- und Adressbuch der Bau- und keramischen Industrie: (Industrie der Steine und Erden, Glas und Porzellan.) 1920-1. Edited by R. Hanel. Vienna: Compassverlag. 328 pp. M 32. Reviewed in *Tonind. Z.* 46, 481(1922).

Taschenbuch für Keramiker. Berlin: Verlag Keramische Rundschau, G. m. b. H. 206 pp. Reviewed in *Z. angew. Chem.* 35, 211(1922).

Glass. H. T. BELLAMY and B. T. SWEELY. U. S. 1,415,980, May 16. A non-electrolytic glass suitable for use as a binder for high-resistance compns. is formed of silicates and borates of Ca and Ba.

Glass. TITANIUM PIGMENT CO., INC. Brit. 176,430, Oct. 29, 1920.  $\text{TiO}_2$  is introduced into glass batches in the ratio of not less than 25% of the whole. E. g., silica 69 parts by wt., borax 10,  $\text{Na}_2\text{CO}_3$  29, CaO 7,  $\text{TiO}_2$  45.

Refractory compositions. BUFFALO REFRACTORY CORPORATION. Brit. 176,436, Nov. 2, 1920. A refractory compn. comprizes Si carbide, flake or cryst. graphite, a flux, and a carbonizing binder, such as tar or molasses. As fluxes, clay, salts, such as borax, metallic or non-metallic oxides, or sulfides may be used. The mixt. is molded in the usual manner and baked at about  $1000^\circ$ . Suitable proportions of the ingredients are 68 pts. of Si carbide, 25 pts. of graphite, and 7 pts. of flux, or of flux and binder. The compn. is suitable for making heat-resisting articles such as crucibles, firebricks, retorts, muffles, furnace cores, tubes, combustion boats, pyrometer tubes furnace linings, and heat-resisting cements.

Refractory compositions. BUFFALO REFRACTORY CORPORATION. Brit. 176,437, Nov. 2, 1920. A refractory compn. for making heat-resisting articles, such as crucibles, comprizes a refractory elec.-furnace product such as fused alumina or silica, flake or cryst. graphite, a flux, and a carbonizing binder such as tar or molasses. As fluxes, clay, salts such as borax, metallic or non-metallic oxides, or sulfides may be used. The mixt. is molded in the usual manner and baked at about  $1000^\circ$ . Suitable proportions of the ingredients are 60 pts. of the elec.-furnace product, 20 pts. of graphite, 12 pts. of binder, and 8 pts. of flux. Cf. preceding pat.

## 20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

Studies of certain fungi of economic importance in the decay of building timbers, with special reference to the factors which favor their development and dissemination. W. H. SNELL. U. S. Dept. of Agr., *Bull.* 1053, 47 pp.(1922). E. J. G.

Plastic compositions (for floor coverings) (Brit. pat. 176,405) 18. Recovery of potash from cement mixtures (U. S. pat. 1,415,572) 18.

Waterproofing concrete. B. F. ERDAHL. U. S. 1,415,324, May 9. Pores of concrete are filled with a metal alginate such as that formed by the action of  $\text{NH}_4$  alginate on lime in the concrete.

Rotary kiln adapted for burning cement. A. B. CARSTENS. U. S. 1,415,990, May 16.

Rotary cement kiln. N. WINQVIST. U. S. 1,415,970, May 16.

Seasoning wood. A. O. CRAIL. U. S. 1,416,269, May 16. Wood is seasoned and shrunk by boiling for 6 hrs. in a 5%  $\text{NaCl}$  soln. and then drying for 42 hrs. in a kiln heated to about  $120^\circ$ .

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

The origin of peat and of coal. HANS HÖFER VON HEIMHALT. *Naturwissenschaften* 10, 113-6(1922).—A review and discussion based on a treatise by Fischer and Schrader (*Entstehung und Chemische Struktur der Kohle*, cf. C. A. 15, 1610, 3202, 3548).

C. C. DAVIS

The microstructure of coal from an industrial standpoint. A. L. BOOTH. *Colliery Guardian* 123, 468-9(1922).—Two coals analyzing resp.: volatile 38.2, 38.1; fixed C 61.8, 61.9; total C 82.2, 81.2; H 5.83, 5.60; O 11.21, 11.93; N 0.76, 1.27; B. t. u. 14,750, 14,750 had entirely different coking properties. In the Mond process, one was a satisfactory coal, the other could not be economically coked. Various grades of coal which were similar microscopically were almost always found similar in coking properties. In this way, by tinting photomicrographs, the coking properties of different coals could be forecasted and controlled without any accompanying chem. analysis. C. C. D.

The sulfur in coal. ED. DONATH. *Brennstoff Chem.* 3, 120-2(1922).—A review of theories of the origin of the various forms of S in coal. The main source is decompn. of proteinoid constituents of the organic deposit, rather than reduction of transported inorg. S compds. W. B. V.

The pyridine extraction of Upper Schleswig coals. FRITZ HOFMANN AND PAUL DAMM. *Brennstoff Chem.* 3, 73-9, 81-91(1922).—The literature of coal extn. is critically reviewed, with conclusions that most investigators have worked with insufficient quantities, and that there is no evidence that  $\text{C}_6\text{H}_5\text{N}$  (A) acts in any other way than as a purely phys. solvent. The first expts. were carried out with a condensation product of pinacolin, with  $(\text{C}_6\text{H}_5)_3$ , and with  $\beta\text{-C}_{10}\text{H}_7\text{OMe}$ , but the quantities of ext. were insufficient. Large lumps of coal were used, since A, even in the cold, causes the lumps to swell and fall apart. The yield was almost as good in the cold as hot, and the com. mixt. of pyridine bases (B) b.  $120\text{-}150^\circ$  gave even better yields of ext. than A, if dehydrated. The coal taken for the large-scale extn. was from the Emma mine in Rybnik; altogether 500 kg. was extd. in 12 batches, yielding 14.88 kg. of cold ext. and 36.75 kg. of hot ext., total 51.63 kg. The exts. were treated with  $\text{Et}_2\text{O}$  and the soln. was shaken with 20%  $\text{H}_2\text{SO}_4$ ; an acid soln. and a solid sepd. The  $\text{Et}_2\text{O}$  soln. was treated with 5%  $\text{NaOH}$ ; an alk. soln. and a thick oil sepd. The neutral oils remaining in the  $\text{Et}_2\text{O}$  were recovered and distd. at 1 mm. up to  $290^\circ$ . Quantities were as follows: insol. in  $\text{Et}_2\text{O}$ , from hot ext. 22716 g., from cold ext. 10022 g.; sol. in  $\text{Et}_2\text{O}$ , from hot ext. 8224 g., from cold ext. 2978 g.; 9012 g. of  $\text{Et}_2\text{O}$  sol. matter was sepd. into 2385 g. bases, 480 g. high-boiling acids, 1044 g. phenols, 350 g. alkali-insol. oils, 6220 g. neutral substances.



which on distn. gave 2968 g. distillate. The latter was refracted and elementary analyses were made, with the following results: satd. hydrocarbons,  $C_{12}H_{24}$ , b. 210-15°,  $d_{20}$  0.8853;  $C_{13}H_{26}$ , b. 225-30°,  $d_{20}$  0.8481;  $C_{14}H_{28}$ , b. 235-40°,  $d_{20}$  0.8511;  $C_{15}H_{30}$ , b. 257-63°,  $d_{20}$  0.8600;  $C_{16}H_{32}$ , b. 278-83°,  $d_{20}$  0.8688;  $C_{17}H_{34}$ , b. 299-95°,  $d_{20}$  0.8674; unsatd. hydrocarbons,  $C_{14}H_{12}$ , b. 154-8°,  $d_{20}$  0.8615;  $C_{15}H_{14}$ , b. 165-70°,  $d_{20}$  0.8623;  $C_{16}H_{16}$ , b. 185-90°,  $d_{20}$  0.8588;  $C_{17}H_{18}$ , b. 205-10°,  $d_{20}$  0.8628;  $C_{18}H_{20}$ , b. 220-25°,  $d_{20}$  0.8812;  $C_{19}H_{22}$ , b. 236-40°,  $d_{20}$  0.9000;  $C_{20}H_{24}$ , b. 245-50°,  $d_{20}$  0.9146;  $C_{21}H_{26}$ , b. 254-8°,  $d_{20}$  0.9217;  $C_{22}H_{28}$ , b. 265-8°,  $d_{20}$  0.9335;  $C_{23}H_{30}$ , b. 274-7°,  $d_{20}$  0.9529;  $C_{24}H_{32}$ , b. 281-4°,  $d_{20}$  0.9593;  $C_{25}H_{34}$ , b. 288-91°,  $d_{20}$  0.9614;  $C_{26}H_{36}$ , b. 293-5°,  $d_{20}$  0.9699. The latter fraction gave a solid picrate, red needles, m. 80°, and left an unattacked oil,  $C_{14}H_{16}$ , b. 289-94°,  $d_{20}$  0.9644. The unsatd. fractions above 275° gave the following color reactions:  $H_2SO_4$  in a water suspension of the oil gives a bluish red, changing to intense blue on addn. of a few grains of  $K_2Cr_2O_7$ ; weakly alk.  $Na_2CO_3$  emulsions of the oil decolorize 1%  $KMnO_4$ , but if the soln. is acidified it becomes cherry-red, beginning at the top. Further examn. of the other extn. products will be reported in other communications.

W. B. V.

The coals of German Austria. M. DOLCH AND G. GERSTENDÖRFER. *Z. angew. Chem.* 35, 181-6(1922).—D. and G. classify the coals according to geologic age, and show for a typical coal of each age the compn., heating value, and products of carbonization. The heating value of the combustible is higher for the older coals. Low-temp. carbonization of some sort is the best means of improving the quality of the younger coals. The coke produced can be easily pulverized, or used domestically; the tar yield will help pay for the process.

ERNEST W. THUELS

The coals of Spitzbergen. P. K. BREUER AND GUSTAV ZIMMERLUND. *Brennstoff Chem.* 3, 98-103(1922).—The extent and character of the known deposits are reviewed. A sample from Sveagruvan, on van Mijen Bay, was examd.; it is classified under Schondorff's group IV., "baking sinter-coal." In the Al coking app. it gave 12.4% low-temp. tar, 81.4% half-coke, 1%  $H_2O$  of decompn., 5.2% gas of 6750 cal. per cu. m. heat content. The ultimate analysis of the dry coal was: C 78.4, H 5.1, N 1.6, S 0.7, O 14.2, ash 10.3, volatile matter 31.5%. Benzene extd. 0.4%; at 250° in the autoclave, 9.8%. The low-temp. tar contained 33% phenols, 0.3% paraffins. The dry half-coke had a heating value of 7277 cal. per kg.

W. B. V.

Increased oxygen absorption by lignite after moistening with an alkali. VON WALTHER AND W. BIELENBERG. *Brennstoff Chem.* 3, 97(1922).—Lignite extd. with a solvent absorbs about 2 cc. more O per g. when moistened with alkali than the raw lignite, probably because of the increased concn. of lignin constituents in the former.

W. B. V.

The formation of phenols from the bituminous constituents of lignite. ED. GRAEFF. *Brennstoff Chem.* 3, 56-7(1922).—Montan wax was sepd. by hot EtOH into wax, resin and residue fractions, the first two then being distd. at a low temp. The distillate from the wax was practically free of phenols. The resin gave 67% of a fluid distillate from which 83% unsaponifiable oil, 4.2% phenols and 3.8% org. acids were sepd. It is therefore concluded that at least in lignite, the resinous constituents of the bitumen are not the principal source of phenols.

W. B. V.

The resin content of montan wax. E. GRAEFF. *Braunkohlen-Brikettindustrie* 29, 297(1921); *Brennstoff Chem.* 3, 59-60.—Montan wax from Webau was treated with warm 90% alc., the wax sepd. from the soln. by cooling, and the resin by evap. the remaining alc. soln. The properties of the 3 fractions, resp., resin, wax and residue were as follows:  $d_{15}$  1.063, 1.008, 1.013; m. p., 72°, 76°, 82°; acid no., 27.5, 49.5, 28; ester no., 28, 61.6, 30; sapon. no., 55.5, 111.1, 58; on distg. to dryness, distillate, 67, 74, 66%; coke, 10.4, 8, 9.2%; gas, 22.6, 18, 24.8%; distillate was dark brown liquid, yellow

buttery, yellow buttery; its sp. gr., 0.981, 0.994, —; acid no., 19.3, 20, 16; ester no., 28.0, 33.6, 28; sapon. no., 47.3, 53.6, 44; paraffin content, 3.26, 44.2, 32%. The resin contents of a no. of samples of montan wax were detd. by 5 extrs. with  $\text{Et}_2\text{O}$ , with the following results: wax from pyropissite, 6.64%; bitumen from Riebeck, 16.54%; Marke Heimann, 46.66%; Bohemian, Marke Corona, 31.54%; Schleswig, Hermsdorf, 67.90%.

W. B. V.

Progress in pulverized fuel firing. F. J. CROLIUS. *Blast Furnace Steel Plant* 10, 337-9(1922).—The code recommended for adoption by the Carnegie Steel Co. in the handling of pulverized coal is presented.

E. J. C.

Burning bituminous coal on Taylor stokers. G. E. WOOD. *Mech. Eng.* 44, 373 (1922).—A good grade of coal with low ash, volatile matter and S-content can be burned efficiently. As the ash, S and volatile matter increase, losses due to combustible matter in the refuse increase.

C. T. WHITE

Burning bituminous coal on Taylor stokers. O. J. RICHMOND. *Mech. Eng.* 44, 374(1922).—A description of the boiler plant is given, also a discussion of the method of operating. When boilers are run at 150% of their rating or above, it is essential that a coal with a high fusing ash (above 2400° F.) be used.

C. T. WHITE

Burning bituminous coal on Type E stokers. R. A. SANDERS. *Mech. Eng.* 44, 374(1922).—A description is given of the boiler plant and of the method of operation. During 15 months service no trouble due to manuf. or design of the stokers has been observed.

C. T. WHITE

Fuel briquets in 1921. W. F. MCKENNEY. U. S. Geol. Survey, *Mineral Resources of U. S.*, 1921, Pt. II, 1-5 (preprint No. 1, publ. May 26, 1922).

E. J. C.

Hydrogenation of acetylene for the preparation of fuel oils. KEIJI ODA. *J. Chem. Ind. (Japan)* 24, 1161-6(1921).—Sabatier's method applied to acetylene gave practically no oil;  $\text{C}_2\text{H}_2$  mainly decompd. into H and C. When a mixt. of equal vols. of  $\text{C}_2\text{H}_2$  and  $\text{H}_2$  was passed over a catalyzer of Ni with a small amt. of Hg at 25-35° there was obtained 51.7% of the theoretical oil yield (36.6 l. of the mixt. gas (calcd. at 760 mm.) gave 8.2 g. of light oil and 3.5 g. of heavy oil b. 200-300°). This special catalyzer is prepd. as follows: 20 g. of pure  $\text{Ni}(\text{NO}_3)_2$ , and 2 g.  $\text{Hg}(\text{NO}_3)_2$  are converted to oxides by heating at 250-300°. 3 g. of the mixt. of these oxides is reduced by H at 300° for 8 hrs. The future of the fuel problem in Japan is discussed.

S. T.

The "national" motor fuel; its actual status and industrial preparation. MARILLER. *Bull. assoc. chim. suc. dist.* 39, 215-31(1921); cf. *C. A.* 16, 1001.—Comm. report which includes the world's production of petroleum, French consumption which was 9,939,182 hectos. in 1920, and French production of other combustibles. Ether costs 20% to 30% more than alc. It has been suggested that the fuel consist of all nationally produced fuels in the proportion in which they are produced, with imported gasoline constituting the remainder of the requirement or: EtOH 10, benzene 5, shale oil 2, Alsatian petroleum 1, MeOH 0.5, and imported gasoline 81.5%. This mixt. forms 2 layers and so a common solvent is sought. Abs. alc. is miscible. Methods of dehydration of alc. are reviewed. This mixt. is hygroscopic and sepn. results on standing. Alc. of 98.2% seps. at -8° and 97.5% at 15°. However, the use of abs. alc. requires less of a common solvent.

I. D. GARARD

The temperatures in gas-producers during the gasification of fuels. HERMANN KOSCHMIDT. *Brennstoff Chem.* 3, 39-42(1922).—The temps. necessary to maintain gasification and drying in a producer fired with fuels of various moisture contents are calcd. from thermal data. For very wet fuels the temps. rise above the fusion point of the ash, which thus becomes a limiting factor in detg. the max. practical moisture content.

W. B. V.

The absence of naphthalene and the presence of naphthalene derivatives in low-temperature tar. FRANZ FISCHER, HANS SCHRAEDER AND CARL ZERBE. *Brennstoff Chem.* 3, 57-9(1922).—A low-temp. tar was prep'd. from Lohberg gas-coal and dist'd. up to 300°. No picrates could be ppt'd. from its alc. soln. The hydrocarbons isolated from the 200-250° fraction, however, gave small ppts. of picrate; fractions 240-5° and 245-50°, corresponding to  $\alpha$ - and  $\beta$ -MeC<sub>10</sub>H<sub>7</sub>, gave the largest quantities. The phenols isolated from the 200-300° fraction ppt'd. no picrates. The total quantity of C<sub>10</sub>H<sub>8</sub> homologs indicated in the tar was not over 1%. The collected picrates were decomp'd. with NH<sub>4</sub>OH and the hydrocarbons passed with H<sub>2</sub> through a tinned-iron tube at 750°; C<sub>10</sub>H<sub>8</sub> was identified as the product. At high temps. in the coke-oven C<sub>10</sub>H<sub>8</sub> and C<sub>10</sub>H<sub>7</sub>OH homologs are reduced and dealkylated to C<sub>10</sub>H<sub>8</sub> as the end-product. Knublauch's picrate method for C<sub>10</sub>H<sub>8</sub> in tar is subject to the error of including these homologs in the weighed ppt. W. B. V.

The carbonization of Sarre coals. BAILLE-BARREILLE. *Compt. rend.* 172, 1580-2 (1921); *Colliery Guardian* 122, 165-6(1921).—The poor quality of coke made from Sarre coals is due to formation of large fissures during the carbonization. Semi-industrial tests made during the past year have shown that small quantities of a good coke can be produced by eliminating the formation of the "screen zone," which is produced by large differences of temp. between interior and exterior of the coking mass. The process consists in: (1) charging crushed fines into an oven whose temp. is maintained below 320°, i. e., the temp. at which Fettkohl begins to decompose, until the difference in temp. between the center and the sides of the coal charge is  $T$  degrees; (2) raising the temp. of the oven at a uniform rate of  $N$  degrees per hour until a temp. of about 750° is reached and this temp. maintained until the charge is completely carbonized. In (1) an even distribution of heat is obtained throughout the whole of the coking mass and the formation of a "screen zone" is prevented by keeping  $T$  and  $N$  sufficiently low. The phenomena of fusion, agglomeration and contraction then take place and only a few large fissures are formed—the fewer as  $T$  and  $N$  are smaller. In (2)  $N$  cannot decrease indefinitely because too slow a rise of temp. between 320° and the fusion temp. of Fettkohl (420°) destroys the faculty of agglomeration. The larger the oven the more slowly must it be heated to prevent the "screen zone" and a certain minimum for  $N$  limits the max. width of the oven beyond which it is not practicable to apply this process. The test ovens were 250 cm. wide, of 500 kg. capacity, charged at 320°, and the coking period lasted 50 hrs. Tests showed that Sarre coke is as good as Ruhr coke. Crushing strength was 350 kg. per sq. cm. (max. required 250) and 80-86% cohesion matter left on 40-mesh screen after drum test (min. required 75%). Yield of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was 22 kg. per ton of coal of 7% ash, as compared with 10-12 kg. with the old process. Low-temp. carbonization favors high ammonia yields. Coking above 700° favors the decompn. of NH<sub>3</sub> into N and H, and it is thus lost. A. R. ALBOUES

By-product coke plant at Midland. ANON. *Blast Furnace Steel Plant* 10, 320-3(1922).—Descriptive. R. J. C.

The determination of degree of swelling on coking. RICHARD LANT. *Brennstoff Chem.* 3, 97-8(1922).—Two pieces of the same coal, each of about 1 cc. vol., are weighed; one is covered with a thin skin of paraffin, the vol. det'd. by immersion in water, and the calcd. sp. gr. used to det. the vol. of the other piece of coal. The latter is then coked in a crucible (being ground and formed into a briquet if necessary to prevent splitting) and the resulting coke is coated with paraffin and immersed in water for vol. detn. The "degree of swelling" is (vol. coke + vol. coal) - 1. W. B. V.

Production of benzine and lubricating oil from coal and crude oils (FANTY, FANTY)  
22. Coal in the Northern Waterberg (TREVOR, DUTTOR) 8.

HANWY, L. C.: *Pulverized Coal Systems in America*. London: H. M. Stationery Office. 115 pp. 5s. Reviewed in *J. Ind. Eng. Chem.* 14, 577(1922); *Chimie et industrie* 7, 830.

*Jahrbuch der Brennstofftechnischen Gesellschaft*. e. V. Vol. III. Halle a. S.: Wilm. Knapp. M 39.

LASUR, LÉON: *Theorie de la combustion et utilisation des combustibles*. Paris: Gaston Doin. 180 pp. 8 fr. Reviewed in *L'age de fer* 38, 1511(1922).

STALEY, R.: *Town Gas Manufacture*. London: Sir Isaac Pitman & Sons. 108 pp. 2s. 6d. Reviewed in *Chem. Age* (London) 6, 621(1922).

Fuel. F. HOSTETTLER. Brit. 176,329, Jan. 20, 1922. Addition to 174,360 (C. A. 16, 1858). Relates to liquid fuel for internal-combustion engines of the kind described in the principal patent and consisting of a mixt. of tar oils, raw oil distillates, and MeOH. The invention consists in using aliphatic, aromatic or hydro-aromatic ketones, aldehydes, or esters, or mixts. thereof, instead of or together with, the MeOH. These substances may be used in the pure or "technical" state, and in proportions not exceeding 10%, addus. of from 3-5% being preferred. In an example, 45 pts. by wt. of tar distillates are mixed with 55 pts. by wt. of raw oil distillates and 8 pts. by wt. of acetone.

Fuel from coal slimes. H. BRUNE and H. HORST. U. S. 1,416,546, May 16. Fluid coal slimes are mixed with coke breeze before settling and H<sub>2</sub>O is expressed from the mixt.

Solidified liquid fuel. H. S. MORE and G. J. ESSELEN, JR. U. S. 1,416,493, May 16. A soln. of pyroxylin in EtOAc and alc. is coagulated in a volatile combustible non-solvent such as additional alc. and this mixt. is combined with a similar soln. of pyroxylin of a concn. near that of coagulation.

Apparatus for catalytic preparation of motor fuels. A. HAYES. U. S. 1,416,291, May 16. The app. is adapted for the treatment of hydrocarbon oils and alc. with a heated catalyst such as Zn, Ni and fire brick in order to form a stable blended fuel mixt.

Briquets from coal. C. H. SMITH. U. S. 1,415,202, May 9. Coal is conveyed through a retort while heated to 440-650° to obtain a partially distd. residue contg., 5-14% volatile hydrocarbon matter and having a somewhat cellular form. This residue is cooled with H<sub>2</sub>O and crushed, mixed with a binder such as pitch to give a mixt. contg. 11-17% volatile matter and briquets of this mixt. are heated to about 1000° to carbonize them. Cf. C. A. 15, 2174.

Vertical furnace-retort. C. H. SMITH and E. B. EDWARDS. U. S. 1,415,061, May 9. The retort is adapted for carbonizing or devolatilizing coal.

Furnace-retort adapted for carbonizing coal. C. H. SMITH. U. S. 1,415,846, May 9.

Furnace-retort adapted for carbonizing coal. C. H. SMITH. U. S. 1,415,201, May 9.

Testing gases. H. ARTHURTON. Brit. 176,396, Aug. 24, 1920. For obtaining a regular sequence of records of the gases in a number of boiler flues with the aid of a single CO<sub>2</sub> recorder, there are provided a no. of single valves, mechanically sep., allocated one to each flue, and electrically operated at given periods and in regular sequence by means of a time switch. A suitable construction is specified.

Preventing accumulation of sticky products on feeding devices of gas producers. C. C. HOFFMAN and J. McCASLIN. U. S. 1,415,238, May 9. The delivery surfaces of the feeding device are treated with a stream of H<sub>2</sub>O.

Apparatus for deodorizing exhaust gases from internal-combustion engines. P. WACHTEL. U. S. 1,415,418, May 9.

Distilling tar or other liquids. J. L. MAJOR. U. S. 1,415,667, May 9. Liquid is fed into the vapor space of the still through pipes passing through the main body of liquid in the still to effect preheating and facilitate discharge of vapors of low-boiling constituents.

Apparatus for distilling tar. C. SCHÄER. U. S. 1,415,056-7, May 9.

Cooling coke. SULZER FRÈRES SOC. ANON. (known as Sulzer Akt.-Ges., Geh.). Brit. 173,761, Jan. 3, 1922. The incandescent coke is conveyed from the distn. plant to a hoist by buckets and the truck and is tipped into a fixed shoot which discharges it into the dry cooling chamber provided. A suitable construction is specified.

Cooling coke. SULZER FRÈRES SOC. ANON. Brit. 173,762, Jan. 3, 1922. The coke is fed in known manner into a cooling chamber and is cooled by a gas, preferably neutral, which is forced in a cycle through the cooling chamber and heat-exchange device. The gas enters the space between upper and lower hoppers and ascends through the descending mass of coke. The cooling of the coke is effected progressively from the bottom, the lower layers being cooled and discharged gradually while the top layers are still incandescent, the fresh coke being added gradually.

Cooling coke. SULZER FRÈRES SOC. ANON. Brit. 173,763, Jan. 3, 1922. Relates to a method of cooling and simultaneously producing water gas, the heat contained in the coke when it is below the temp. at which water gas is formed, namely, 600-700°, being utilized to produce the necessary steam. A suitable construction is specified.

Coking retort oven. J. BECKER. U. S. 1,416,322, May 16.

## 22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Oil in the quadrant formation in Montana. O. W. FREEMAN. *Eng. Mining J.-Press* 113, 825-7(1922).—The present development comprises 70 producing wells at Cat Creek, which is served with a pipe line, five at Soap Creek, and two in Devils Basin. The oil from Cat Creek is said to be more than 50% gasoline and has neither a paraffin nor an asphaltic base. This petroleum contains no lubricating oil. A heavy black petroleum is produced at Soap Creek and Devils Basin. A detailed discussion is given of the geologic relationships with reference to the probable origin and diverse nature of the oils.

E. T. ERICKSON

The oil supply of the U. S. *Bull. Am. Assoc. Pet. Geologists* 6, 42-6(1922).—A review of the producing, probable, and possible oil-bearing regions of the U. S. by a joint committee composed of members of the American Association of Petroleum Geologists and of the U. S. Geol. Survey. Their inventory estimates that 9 billion barrels of oil recoverable by methods now in use remains in the ground in this country Jan. 1, 1922. A table of estimates is given of oil reserve by states or regions. R. T. GOODWIN

A preliminary report on the oil shales of Kentucky. W. R. JILLSON. *Ky. Geol. Survey, Econ. Papers on Ky. Geol. Series* 6, 1-38(1921).—With the composite outcrop acreage of Devonian black shale in Ky. as 609,920 acres and an empirically assumed thickness of 20 ft., a total tonnage figure may be obtained for this state that is stupendous. The av. oil content of 16.08 gals. per t. when multiplied by this tonnage gives a possible recoverable quantity of tarry oil of over 12 billion barrels. *Distn. and analysis*

of over 20 samples of the Devonian black shale from almost as many different counties, gave the following av. results: oil content 16.08 gals. per t., d. 2.173, wt. 129.37 lbs. per cu. ft., S 1.5-4.15%, combustible matter 10.26-16.72%, fixed carbon 4.61-10.06%, ash 73.42-83.90%.

R. T. GOODWIN

**Sampling of oil shale.** CHAS. C. STARR. *Eng. Mining J.-Press* 113, 873-7(1922).—On account of the low per ton value of the material, accuracy in the sampling of oil shale is important. Sampling may be made by means of diamond drill or careful surface sampling of all strata of possible commercial value. Surface sampling should be accomplished by a careful study of the strata to det. uniformity or lack of uniformity, oil content and other characteristics. If the weathered outcrop is cleaned off, leaving a fresh appearing shale, strata of good or medium grade of shale may be sampled directly on the surface. The upper strata of rich shales are variable in their surface structure and oil content. Sampling from this type of shale should be done in numerous places to obtain its true av. value. The average error of properly taken surface samples is about 2.5%.

R. T. GOODWIN

**Significance of the interpretation of the chemical analyses of seepages.** J. E. HACKFORD. *J. Inst. Petroleum Tech.* 8, 193-213(1922).—The paper is suggestive in the interpretation of the character of an undrilled petroleum as indicated by the analyses of visible solid and liquid seepages and gas. Analytical data of seepages in their relationship to underlying petroleum bodies are not given but instead the reader infers this by certain facts known to occur in the Mexican oil fields. H. considers a petroleum as dependent upon the nature of the original org. matter and geologic conditions. The low N and high S-content of the Mexican petroleum are ascribed to an algal origin. The secondary effect of S which occurs normally in the dolomitic reservoir increases also the asphaltic content and the gravity of the petroleum. This increase depends upon the amt. of S, which in turn is influenced by the amt. of dolomite. Data are given to show this relationship. Analyses of gases are also given to show the possible relationship of the H, N, and  $H_2S$  content with type of petroleum.

E. T. ERICKSON

**Detection of benzene in benzine.** P. SCHWARZ. *Chem.-Ztg.* 46, 401(1922).—Five cc. of the benzene is added to 2 cc. of a mixt. of equal vols. of aniline and 94-96% (vol.) EtOH. If no  $C_6H_6$  is present, a lower liquid layer ( $PhNH_2$  and EtOH) forms. As little  $C_6H_6$  as 5% in the benzene effects complete soly. The fraction b. 80-110° may be used to advantage, rather than the benzene itself.

W. F. FARAGHER

**The analytical distillation of petroleum and its products.** E. W. DEAN, H. H. HILL, N. A. C. SMITH, AND W. A. JACOBS. *Bur. Mines, Bull.* No. 207, 82 pp.(1922).—The methods of the Bur. Mines for the distn. of petroleum and its products are described. Routine methods for distg. crude oil at atm. pressure and in a vacuum, for distg. lubricating oil, and special distn. methods are given. Methods for detg. sp. gr. and viscosity are included, together with a discussion of the instruments used. The cloud test is described. Tests for water, and methods of dehydration are given. The construction of elec. heaters is discussed.

E. H. LESLIE

**Properties of typical crude oils from the producing fields of Northern Texas, Northern Louisiana and Arkansas.** E. W. DEAN, M. B. COOKE AND C. R. BOFF. *Bur. Mines, Repts. of Investigations*, No. 2293, 50 pp.(1921).—Twenty-eight crude-oil samples were analytically examd. The report tabulates sp. gr., distn. data, percents of S, Saybolt viscosities at 70° F. and at 100° F., results of pour tests, percents of gasoline, and results of carbon-residue tests. The cloud tests of vacuum distn. fractions are given. For comparison the results of a similar examn. of eleven oils from other fields are given.

E. H. LESLIE

**Production of benzene and lubricating oil from coal and crude oils.** WILLY FÄRY

AND ALFRED FABER. *Chem.-Ztg.* 46, 377-9(1922).—The cracking process patented by Blummer (Ger. patents 338,846 and 340,901; also several pending applications) is recommended for making motor fuel and lubricant from lignite tar, producer tar or shale oil produced in Germany, or from imported low-grade petroleum products such as gas oil or Mexican crude oil. The oil is sprayed into a lower section of the app. (decompn. autoclave) from which it passes to a superimposed chamber filled with Raschig rings and surrounded by a bath of molten metal. The construction is such that rapid circulation of the molten metal along the wall exposed to the furnace is insured. The app. is small, but has a large daily capacity. The following yields are claimed: from lignite producer tar: 30.2% benzine, 34.4% lubricating oil and paraffin, 16% asphalt, 16.9% gas and loss and 2.5%  $H_2O$ ; from shale-oil (Middle Germany): 32.5% benzine, 31.0% lubricating oil and paraffin, 15.4% asphalt, 20.5% gas and loss, and 0.5%  $H_2O$ .  
W. F. FARAGHER

Natural-gas gasoline in 1920. E. G. SIEVERS. U. S. Geol. Survey, *Mineral Resources of U. S.*, 1920, Pt. II, 289-300 (preprint No. 30, publ. Apr. 28, 1922).

E. J. C.

Composition of paraffin wax (FRANCIS) 10. Origin of Alberta tar sands (COVENS) 8. The determination of aromatic hydrocarbons in distillation fractions of mineral oils (WATERMAN, PERQUIN) 7. Effecting chemical reactions (Brit. pat. 176,438) 13. Recovering condensable substances from gases (U. S. pat. 1,415,058) 13.

BUDOWSKI, J.: Die Naphthensäuren. Berlin: Julius Springer. Reviewed in *Petroleum Z.* 18, 464(1922).

KLEIN, N.: Het oliestoken. Rotterdam, Amsterdam: Uitgave u. d. Vereniging van Scheepswerktuigkundigen. 148 pp. fr. 4.25. Reviewed in *Chem. Weekblad* 19, 87(1922).

Cracking hydrocarbon oils. C. ELLIS. U. S. 1,415,232, May 9. Kerosene oil or a heavier oil is passed through metal tubes in which it is heated to a cracking temp. at a single passage and the products thus formed are passed through a larger pipe or drum without raising their temp. and without reducing the temp. below the decomp. point, both these operations being conducted under pressure.

Hydrogenizing hydrocarbons. A. J. STEPHENS. Brit. 174,106, Aug. 12, 1920. Satd. hydrocarbon mixts. similar to com. petroleum products are produced by vaporizing the volatile matter of an unsatd. hydrocarbon mixt. and condensing to a liquid in the presence of H under pressure, say 4 or 5 atms. A catalytic material such as Ni may be provided at the point where condensation occurs, but the ordinary metal condenser walls may in some cases have sufficient catalytic action. The raw material, such as a petroleum waste or by-product, or the product of low-temp. distn. of coal, may be contained in a still heated by fuel or internally by steam or inert gases. Within or outside the still the hydrocarbon vapor is mixed with H obtained from a catalytic dehydrogenator supplied with natural gas or still gases. A pump forces the mixt. under the required pressure to the condenser, any uncondensed gas being returned to the dehydrogenator. Cf. 166,989 (C. A. 16, 643) and 170,140 (C. A. 16, 1148).

Distilling oils. T. E. ROBERTSON. Brit. 176,099, Nov. 26, 1920. In topping or distg. oils by passing them through heated tubes and then into a vapor separator, the tubes are arranged so that the oil passes mainly counter-current to the hot gases. A suitable construction is specified.

**Distilling oils.** T. E. ROBERTSON. Brit. 176,100, Nov. 26, 1920. In distg. or topping petroleum oils, the oil is heated by passage from an inlet through tubes embedded in fire-brick blocks in the roof of a furnace and then through banks of tubes over which the furnace gases pass. The heated oil is passed into a separator, from which the vapors pass to a condenser. Separators for the vapors may be arranged between the tubes in the furnace roof and the first bank of tubes and between the sep. banks of tubes. A suitable construction is specified.

**Distilling oils.** POWER SPECIALTY CO. Brit. 176,101, Nov. 26, 1920. In app. for distg. or topping oil in which the oil is pumped upwards through a bank of tubes through which furnace gases pass downwards, and then through a hotter bank of tubes and is delivered to a vapor-sep. chamber, a portion of the oil from the base of the chamber is re-circulated through the hotter bank of tubes and returned to the separator. A suitable construction is specified.

**Distilling oils.** POWER SPECIALTY CO. Brit. 176,102, Nov. 26, 1920. In fractionally distg. oil, the oil is pumped through a zigzag tube in the furnace roof and passes in succession through a no. of banks of tubes heated by the furnace gases. Between each set of tubes the oil passes into a vapor-separator contg. spreaders. A suitable construction is specified.

**Improving oil in wells.** E. C. HALLMARK. U. S. 1,415,552, May 9. Mech. features of blending gas and oil before final delivery from wells.

**Concentrating sludge acid.** I. HECHENBLIKNER and T. C. OLIVER. U. S. 1,415,443, May 9. Sludge acid from treatment of petroleum with  $H_2SO_4$  is first concd. by one stage of heating and then heated to a higher temp., preferably about  $285^\circ$ , to effect further purification.

**Apparatus for petroleum distillation.** C. A. JOURTT. U. S. 1,415,876, May 16.

## 23—CELLULOSE AND PAPER

CLARENCE J. WEST

**Studies on cellulose. I.** Application of H capillary viscosimeter. MICHIMARO NAKANO. *J. Chem. Ind. (Japan)* 24, 918-26(1921).—By means of H capillary viscosimeter (Gibson and Jacobs), N. investigated various factors which change viscosity of cellulose dissolved in cuprammonium soln. The viscosimeter is slightly modified so that the soln. can be protected from air and light. All detns. were made in a const.-temp. bath ( $\pm 0.1^\circ$ ). S S filter paper (No. 590) was dried in a desiccator and used as the cellulose and dissolved in cuprammonium soln. to make a 0.5%. Viscosity detd. at  $25^\circ$  shows that it is practically const. for 2 hrs., during which it can be detd. with great accuracy. Protection of the soln. from light and air does not prevent gradual decrease in viscosity after long standing. The change is perhaps due to the trace of air which finds its way into the soln. as well as H. Effect of heating the soln. for 4 hrs. at the different temps. shows the following results:  $100-5^\circ$ , 2.20 (viscosity of the soln., compared to that of the solvent),  $120-5^\circ$ , 2.14;  $140-5^\circ$  1.87,  $160-5^\circ$ , 1.62;  $180-5^\circ$  1.51, while the control was 2.26. Effect of mercerization on viscosity was studied with cotton cellulose (10 g. of cotton to 200 cc. NaOH solns. for 24 hrs.). The results are: 0% NaOH 4.22; 11% 3.59; 17% 3.03; 20% 2.01. S. T.

**Some experiments on the separation of fatty acids and resin acids in the liquid resin from the sulfate (pulp) process.** ASTRID CLEVE VON EULER. *Archiv. Kemi. Mineral. Geol.* 8, No. 4, 21 pp.(1921).—The liquid resin obtained as a by-product in the sulfate pulp process owes its consistency to the presence of a large amt. of unsatd.



fatty acids, often as high as 50-60%. Analytical methods for their sepn. from the resin acids are known, the best being Twitchell's method, which depends on the fact that resin acids, in contradistinction from fatty acids, do not form esters with alc. when HCl gas is passed into a soln. of the acids in alc. The purpose is to find a method which could be used on a com. scale. Twitchell's method is too expensive and difficult of operation and the literature gives no guide to a more suitable method. E. experimented along the following lines: (1) Ca resinate by itself is easily sol. in alc., while Ca oleate is sparingly sol. However, when the 2 are mixed, as in liquid resin, no appreciable sepn. was effected. (2) The Ca soaps of the mixed acids were dissolved in ether and partial pptn. of the ether soln. with alc. was attempted. Results were negative. (3) The soly. of the Pb salts was investigated but without leading to anything of value. (4) Partial pptn. of the Na soaps of the mixed acids with  $\text{CaCl}_2$  was tried. Some little difference in the fractions was noted. (5) Fractional pptn. of the fatty acids in alc. soln. by  $\text{CaCl}_2$ , each addition of  $\text{CaCl}_2$  being followed by an equiv. amount of NaOH. Some sepn. was obtained and the properties of the various fractions were studied, but the results were not good enough to warrant any hope of a com. method being developed. The 1st fraction contained about 10% less resin acids, and the last about 10% more, than the original material. Much more acid is pptd. in the 1st and 2nd fractions than is calcd. to combine with the  $\text{CaCl}_2$  added (in many cases more than twice as much). E. dismisses the possibility of an acid salt being formed and is of the opinion that it is a soly. phenomenon. The problem of com. sepn. remains unsolved. S. G.

Fastness of dyeings to gases and the detection of formaldehyde. P. HEERMANN. *Textilber.* 3, 101-21(1922).—The detection of  $\text{CH}_2\text{O}$  in paper or cardboard used for boxes is best accomplished by placing a piece of the sample directly into a soln. of fuchsin- $\text{SO}_2$ . Lignin from wood-fiber gives a pink color after long standing, whereas the change is rapid if  $\text{CH}_2\text{O}$  has been used as a preservative in the glue, etc. employed at the box-factory. The method of Cohn (*C. A.* 16, 222) is just as sensitive. Pieces of paper are placed into the soln., or are moistened with it. In order to avoid the confusion resulting from the discoloration of the paper by the  $\text{H}_2\text{SO}_4$ , the color should be observed after a few secs. Fuchsin- $\text{SO}_2$  soln. may be used for quant. detns. (colorimetrically) or the method of Orchard may be employed (weighing Ag formed by reduction of alk.  $\text{AgNO}_3$ ). W. F. FARAGHER

Spent sulfite liquor as a fertilizer (SODERBAUM) 15. The importance of carbohydrates in present-day economy (HAAS) 28. Dyeing cellulose acetate (Brit. 176,535) 25. Nitrocellulose sheets or films (U. S. pat. 1,415,059) 5. Cellular alginate composition (U. S. pat. 1,415,850) 18.

Cellulose ethers. J. M. DONOHUE. U. S. 1,415,023, May 9. Cellulose is soaked in NaOH soln. until mercerized, powd. NaOH is then mixed with the product, excess soln. is pressed out and the material is etherified, *e. g.*, by heating in an autoclave with EtCl.

Webs, sheets and molded articles of fibrous cellulose. C. F. CROSS. Brit. 173,971, Jan. 4, 1921. Fibrous hydrated cellulose produced by the process described in 126,174, (*C. A.* 13, 2288) and formed into sheets on a paper machine, or into molded articles upon hollow or shaped molds, are reverted back to fibrous cellulose during the final stage of felting the fibers on the paper machine, or on the mold, by treatment with a reagent contg. an acid or acid group in sufficient quantity to react with the whole of the soda present. Weak acids, such as  $\text{HOAc}$  or  $\text{H}_2\text{SO}_4$ , or the more easily dissociated salts of the stronger acids, such as  $\text{Al}(\text{SO}_4)_3$ ,  $\text{ZnCl}_2$  or  $\text{ZnSO}_4$ , or waste sulfite liquor, may be used.

**Decomposing waste sulfite liquor.** K. MÖRCH. U. S. 1,415,843, May 9. The liquor is passed continuously through a container in which the temp. and pressure are regulated to form a ppt. of  $\text{CaSO}_4$  and org. substances.

**Waterproof paper.** L. KIRSCHBRAUN. Brit. 174,114, Sept. 7, 1920. In the production of a waterproof paper or felted web, according to the process described in 151,029 (C. A. 15, 598) the emulsion is produced by a continuous process. The clay suspension, or the emulsified product of a previous operation, is heated to the m. p. of the asphalt, and the molten asphalt, or asphalt and clay, added with rapid agitation. The mixt. is produced and the supply maintained in a mixer having, e. g., helical blades. As the mass tends to thicken, water of suitable temp. is added to maintain the desired viscosity and temp. For binding media of high m. p., the emulsification is carried out in closed mixers under pressure. Cf. C. A. 16, 1013.

**Insulating paper.** FUSAICHI TAGAWA. Jap. 39,173, July 7, 1921. Paper is passed through a paste prepd. by mixing globulin 100,  $\text{H}_2\text{O}$  500 and borax 10 parts with shellac 70,  $\text{H}_2\text{O}$  500 and borax 14 parts and satd. lime water 60 parts, piled to suitable thickness, pressed with hot hydraulic press and calendered.

**Apparatus for preparing paper-pulp.** C. W. SHARTLE. U. S. 1,415,902, May 16

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

**Destruction of explosives and ammunition.** ANON. Z. *ges. Schiess-Sprengstoffw* 17, 15(1922).—All detonators, primers, etc., should be isolated from explosives and burned in special app. Not more than 50 kg. of high explosive should be burned at one time and only when spread in a thin layer and against the wind. Only one kind of explosive should be burned at once, and the ground cooled with water before a second charge is burned in the same place. C. G. STORM

**Impurities in synthetic potassium nitrate used in black powder.** A. JUNK. Z. *ges. Schiess-Sprengstoffw* 17, 1-5(1922).—During the last 3 years of the World War an unusual number of explosions occurred in the manuf. of black powder in Germany, which could not be entirely attributed to mech. impurities in the charcoal and S. The  $\text{KNO}_3$  was made chiefly by conversion of synthetic  $\text{NaNO}_3$  (from synthetic  $\text{HNO}_3$  and electrolytic  $\text{NaOH}$ ), smaller amts. being made from "Norwegian saltpeter,"  $(\text{Ca}(\text{NO}_3)_2)$ , or directly from  $\text{HNO}_3$  and electrolytic  $\text{KOH}$ . A careful study of impurities was made on 33 samples from various factories, including material of synthetic origin and that made from Chile  $\text{NaNO}_3$ . The synthetic material was found to be the more pure. The max. content of impurities found was as follows: total Cl 0.06%,  $\text{KClO}_4$  0.055%,  $\text{KNO}_2$  0.05%,  $\text{NH}_3$  less than 0.01%,  $\text{KClO}_3$  not weighable, mech. impurities 0.02-0.06%, org. impurities not weighable,  $\text{SO}_4$ , Ca, Mg, and heavy metals not weighable, except Fe trace, moisture less than 0.1%. All samples met requirements of both German and French specifications. Synthetic black powder compns. contg. from 0.1% to 5%  $\text{KNO}_3$  were tested for sensitiveness to impact and ignition temp. Results were not affected by less than 0.5%  $\text{KNO}_3$ , while 5% was necessary for a distinct effect. The methods of analysis are discussed. In *dein. of KClO*, it is important that the temp. of heating for conversion to KCl should not exceed  $600^\circ\text{C}$ .;  $1/2$  hr. at this temp. is sufficient. At  $550^\circ$  conversion is very slow; at  $700^\circ$  loss from volatilization results. C. G. STORM

**Comments on "the new German blasting cap of Schulze."** C. BUNGE. Z. *ges. Schiess-Sprengstoffw* 17, 18(1922).—B. asserts that the comparison tests described

by Bomborn (*C. A.* 16, 1867) lead to erroneous conclusions, as the ordinary No. 8 caps used for comparison were apparently not of standard strength, a condition characteristic of German blasting caps made since the War. A lead plate test alone is not conclusive but should be supported by lead block expansion tests. The results obtained in the lead plate test with the Schulze caps are due mainly to the deep indentation in the base of the cap, and not to increased density of charge. The effects obtained with concave blasting charges have already been noted by Neumann (*C. A.* 8, 2621). Also, caps have for many years been made with more or less concave base, and the local effect produced thereby is well known.

C. G. STORM

Testing for explosibility. A. MOYE. *Chem.-Ztg.* 46, 69(1922).—The terrible explosion at Oppau will perhaps never be fully explained, because of the lack of witnesses. But it may be assumed from previous investigations and from the claims made by specialists that the loosening with the aid of explosives of the rock-like mass of ammonium sulfonitrate, hardened by surface soln. and recrystn., was not the cause of the catastrophe. Even pure  $\text{NH}_4\text{NO}_3$  is exploded only by means of the strongest initiators; ammonium sulfonitrate, on the other hand has been shown by the expts. of the Badische Anilin- und Sodafabrik to be non-explosive with the strongest detonating charges ordinarily used. Blasting of the ammonium sulfonitrate in storage had failed to produce any explosion of the salt up to the day of the catastrophe; and it has since been shown that all ordinary blasting conditions fail to produce explosion. The possibility of an unusually strong explosive having been used for blasting the salt is not likely, since the pulverizing and scattering of the brittle mass by such an explosive would render it less efficient than a weaker explosive. Furthermore, the detonator used with the explosive would not come in contact with the salt. It would seem advisable to use in such investigations, not only ordinary explosives, but also the strongest explosive possible. This is probably a paste of liquid oxygen and acetylene, obtained according to Anschütz (cf. Hofmann, "Lehrbuch der anorganische Chemie," 1920, p. 335) by passing dry acetylene into liquid air. This mixt., which explodes on contact with a flame, should be "by far the strongest of all explosives." Theoretically, 1 vol. of acetylene combines with 2.5 vols. of O and according to Hofmann and others, 1 cu. m. of acetylene at 15° and 760 mm. pressure liberates 13,000 cal. As 1 kg. of liquid air, (less than 1 liter), contains 232 g. O, this quantity requires 75 g. acetylene, or 68 l. at 15° and 760 mm. By the explosion, according to the above equation, 1 vol. of acetylene yields 2 vols. of  $\text{CO}_2$  and 1 vol. of water vapor, which is expanded to ten times its normal vol. by the resulting temp. of 2700°. Thus, from 1 kg. of liquid air there results a volume of 2040 l.

C. G. STORM

Testing for explosibility. F. CROTOGINO. *Chem.-Ztg.* 46, 117(1922).—The proposal of Moye (preceding abstr.) for improving the testing for explosibility of products having free energy, by using the most brisant explosive as initiator is commendable. The initial explosion can, however, be greatly increased in violence, not only by using the strongest explosive, but by obtaining the cumulative explosive wave resulting within the mass of the product being investigated by means of two charges on opposite sides (D. R. P. 318,059). It can be shown by a well known experiment, that two simultaneous explosions heat the air to incandescence at the point where the explosion waves meet. The concussion produced by the explosion waves coming from two sides is of much higher degree than that from a single charge. It is, therefore, recommended that a substance which contains free energy but cannot be exploded by the strongest means, be tested as follows: Not too small a sample of the substance is formed into a cube, first under suitable compression, in order to approach conditions of mass storage, and second, loose, in order to ascertain the effect of enclosed air. Exactly in the middle of each of two opposite sides a cartridge of highly brisant explosive is inserted, each primed with

a strong detonator. The two cartridges are detonated simultaneously by means of a symmetrically placed detonating fuse, a lead tube filled with trinitrotoluene, or by elec. detonators. In this manner, the explosion waves from the two cartridges meet in the interior of the material under test, the shock produced being far greater than that produced by the most brisant single charge. It is inconceivable that a substance which has withstood this test with a sufficient charge and under varying conditions without explosion, can be brought to explosion by any other means. C. G. STORM

Explosion at the Saarwellingen dynamite factory. ANON. *Z. ges. Schiess-Sprengstoffw.* 17, 14(1922).—This plant manufactures safety explosives for mining purposes. On Dec. 6, 1921, a small flame, rapidly increasing in size, was noted coming from one of the TNT melting kettles, which was heated by means of a steam jacket to 100°. A violent explosion followed, killing 13 on-lookers. The cause of the ignition is unknown, but it is suggested that the behavior of TNT is uncertain when it is heated for a long time in contact with metals. C. G. STORM

VEROLA, P.: *Chimie et fabrication des explosifs*. Paris: Armand Colin. 202 pp. fr. 5, bound fr. 6.

Explosive. J. R. MARDICK. U. S. 1,415,889, May 16. Black blasting powder is glazed with finely divided amorphous electrolytically produced graphite partially to waterproof it, and improve its sensitiveness and uniformity of burning.

Priming composition for small-arms ammunition. H. T. PECK. U. S. 1,416,121, May 16. Trinitroresorcinol 15, Pb thiocyanate 20,  $\text{KClO}_3$  50 and the Pb salt of trinitroresorcinol 15% are used together. U. S. 1,416,122 specifies a similar compn. in which diplumbic di-tri-nitroresorcinol is used. U. S. 1,416,123 specifies a similar mixt. contg. Hg fulminate instead of the Pb nitroresorcinol compds.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

The fastness of dyeings to gases. E. RISTENPART. *Textilber.* 2, 213(1921).—By fastness to gases is meant ability to withstand, during storage and sale, the action of those gases which are sometimes found in the air, *e. g.*, products of combustion of coal, oil or gas, and oxides of N. Fading or change of color takes place in the dark, which differentiates this change from those due to light. An unusual case of this kind was found in a lot of brown hose, which became discolored during storage. Expt. showed that the same changes in the dyeing were effected by the products of combustion of a Bunsen burner. Since the hose in some of the cartons were found to be discolored, and had not been in rooms in which gas was burned, it became necessary to find another source for the substance causing the damage. This was found to be the cartons themselves, which contained  $\text{CH}_4\text{O}$ . Strips of filter-paper moistened with fuchsin- $\text{SO}_2$  soln. became red after 14 days when placed in the cartons, whereas similar strips placed in closed vessels did not change. Since strips exposed to the air of the laboratory became red also, the proof of the presence of  $\text{CH}_4\text{O}$  in the cartons is faulty.

W. F. FARAGHER

Dyeing linen, half-linen, and cotton (blue). JULIUS WERNER. *Textilber.* 3, 136-7(1922).—Cloth for workmen's garments is dyed as follows: An indigo ground is topped with S blue, or a S blue or black ground is topped with indigo. These dyeings

are faster to light and washing than those made by topping an indigo ground with a substantive dye.

W. F. FARAGHER

**Harmful action of strong acids on wool.** M. BECKE. *Textilber.* 2, 194-5, 213-5, 230-1(1921); cf. C. A. 13, 2803; 14, 1760.

W. F. FARAGHER

**The dyeing of straw and hemp.** L. G. HAYES. *Color Trade J.* 8, 28-9(1921).—These fibers resemble jute in dyestuff affinities and may be dyed with basic colors without a mordant, acid or direct colors as required by fastness.  $H_2O_2$  or  $Na_2O_2$  should be used in bleaching as Cl is unsuitable. Acid and basic colors with AcOH are principally used for straw. Hemp and chip are generally dyed with direct colors but basics are sometimes used. A list of 57 suitable dyes is given.

CHAS. E. MULLIN

**Dyeing cotton hose.** JULIUS SCHMIDT. *Textilber.* 3, 9-11(1922).—Dyeing of hose can be considered under 2 divisions: dyeing colors and dyeing blacks. For colors, the hose are bowked, rinsed, soured with HCl and thoroughly rinsed. Bleaching is necessary for white and light shades. Dyeing should be done promptly in order to avoid the unlevel shades which result when the hose dry unequally in the air. Direct dyes are preferred and are applied in the vat or, for large lots, in app. Seams dye uniformly if the bath is exhausted very slowly. Deeper shades are produced best by developed or S dyes, since these dyeings are fast to washing. Turkey red oil or monopol soap should be added when S dyes are used. In order to avoid bronze shades, care must be exercised in adding salt or Glauber salt.  $Na_2S$  is used in the first rinse, and AcONa to the last. Mercerized hose are dyed with substantive dyes in a soap bath, then without rinsing put into a bath which contains 5-10 g. tartaric acid per l. or an equiv. of HCOOH or lactic acid. After poling for 15 mins., centrifuging and drying at high temp., the hose have a silk-like handle. For black dyeings, substantive dyes are used only for cheap hose. Mercerized hose are dyed with developed dyes (e. g., Oxydiaminogen OT, developed with diamines). S dyes give good results when certain precautions are observed: the dye must be dissolved properly; the bath must not be too strong; salt must be added sparingly to standing baths, in order to avoid bronzing; sufficient quantities of  $Na_2S$  and  $Na_2CO_3$  must be added; the goods must be kept immersed; temp. must be 60-70°, in the vat, agitation must be thorough, and goods must not form bunches; and drying must be effected at a low temp. Aniline black plays an important role in this field also.

W. F. FARAGHER

**Dyeing of deaminated wool.** W. W. PADDON. *J. Phys. Chem.* 26, 384-9(1922).—The expts. verify the work of Bentz and Farrell (cf. *J. Soc. Chem. Ind.* 16, 405) and furnish quant. data regarding the dyeing of deaminated and of ordinary wool by the typical acid dyes Orange II (duPont) and Lake Scarlet R (Nat. Aniline and Chem. Co.). The quant. expts. show that amino groups in wool play no part in the dyeing of that fiber by acid dyes.

L. W. RIGGS

**Dyeing wool with chrome-mordant dyes.** A. GANSWINDT. *Textilber.* 3, 151-3 (1922).—Historical account, covering the approx. 50 yrs. following the introduction of the process employing these dyes.

W. F. FARAGHER

**Injuries caused during bleaching by metal impurities.** W. KIND. *Textilber.* 3, 131-4(1922).—Cu, Cu soaps, Fe and Fe rust catalyze the oxidation of cellulose by hypochlorite solns. Tables show the decomp. action of various metals and compds. on hypochlorite solns. Photographs of damaged fabrics are included.

W. F. F.

**Dyeing wool and worsted pieces.** JOS. A. KNOX. *Am. Dyestuff Rep.* 10, 369-72 (1922).—The dyer needs to know all the treatments the goods have received, from the time the wool is oiled for carding until the delivery of the goods at the dye house. Water, soaps, mordants, temps. and the many causes of cloudiness are discussed.

L. W. RIGGS

**Two-effect and multi-colored effects on woolen piece-goods.** M. KÖNIG. *Textilber.* 2, 178(1921).—Advantage is usually taken of the increased affinity for certain dyes, of fibers which are treated with Cl, acids, mordants, etc. Mixts. of such treated wool and untreated wool are mixed before spinning. Thiocyanates increase the affinity of wool for acid after-chrome and mordant dyes, while 25% of  $\text{Na}_2\text{S}_2\text{O}_3$  and 16% of 22° B $\phi$ . HCl (both on the wt. of the wool), if used at 50° for 1-1.5 hrs., decrease the affinity of wool for acid, substantive and mordant dyes. The latter treatment increases the affinity for basic and vat dyes. By controlling the compn. of the bath to enhance the differences between the treated and untreated wool, the pieces show colors of marked contrast.

W. F. FARAGHER

**Two-color effects by printing vat-dyes.** W. KIELBASINSKI AND W. NAPALKOW. *Textilber.* 2, 281-2(1921).—A note dated April 2, 1914. If the soln. used has insufficient alkali and reducing agent, and is then printed with an alk. soln. of reducing agent, light and heavy shades are obtained by steaming for 5-7 min. in a Mather-Platt, washing and soaping strongly.

W. F. FARAGHER

**Substantive dyes and substantive dyeings.** R. HALLER AND HORST RUSSINA. *Kolloid-Z.* 30, 249-53(1922).—Congo rubin (A), Congo Corinth G (A) and Diamine blue 3R (C) were titrated in 0.1% soln. with  $\text{TiCl}_3$  by a slightly modified Knecht method. Assuming mol. wts. of 697, 697 and 743, resp., the %'s of pure dye in the com. samples were 44, 30.7 and 42.07. Substantive dyeings are produced satisfactorily only when the dye exists in a definite degree of dispersion. In general, particles of a wide range of sizes are present, the %'s of those of a favorable size for dyeing varying with the dye and the conditions of the bath, e. g., temp., concn. of electrolytes, etc. Exhaustion of dye-baths was checked in the following manner: Twenty-five-cc. portions of a 1% soln. of the com. dyes were dild. with 225 cc. and 200 cc. of distd.  $\text{H}_2\text{O}$ . Into each cold bath was placed 2 g. of bleached cotton. The temp. was raised gradually to 90° by a water bath, and maintained there for about 1 hr. After the bath had been maintained at 90° for 0.5 hr., 25 cc. of 0.1% soln. of NaCl was added to the second bath. The vol. of each bath was kept about const. by the addn. of distn.  $\text{H}_2\text{O}$ . The dyed samples were rinsed with equal vols. of dil. NaCl, and the washings added to the appropriate baths. The wt. of dye not removed by the cotton was detd. by titration. The results follow (first figure for dye alone, second for dye + added NaCl). Congo rubin, 69.2 and 49.7%; Congo Corinth, 63.2 and 33.2%; Diamine blue 3R, 60.5, and 49.0%. Dialysis through S. & S. thimble against distd.  $\text{H}_2\text{O}$ , gave the % of NaCl in the samples as follows: Congo rubin, 34%; Congo Corinth 23%; and Diamine blue 3R, 22%. The differences in the behavior of Congo rubin and Congo Corinth are striking, and are attributable to differences in the degrees of dispersion. Study of other isomeric dyes may give an answer to the cause of the differences in the degrees of dispersion in  $\text{H}_2\text{O}$  solns.

W. F. FARAGHER

**Testing and standardizing dyes.** E. GREENHALGH. *Am. Dyestuff Rep.* 10, 381-3(1922).—The fixtures and app. of a modern dye-testing lab. are suggested. Methods of sampling and general directions for making tests are given. Six processes are described in detail for the following classes of dyes: (1) Azo acid dyes such as Croceins, Ponceau and Acid Orange 11, (2) Phthaleins, Eosin, Acid Magenta, etc. (3) Sensitive colors particularly dyes derived from the tetrahydroxyanthraquinones. (4) Colors which are affected or unduly pptd. by vitriol, also chromed colors which are destroyed by using bichromate along with vitriol. (5) Colors applied by the meta-chrome process. (6) Colors dyed on chrome-mordanted wool such as Alizarin Green and Blue Black. In the reduction of all colors used for wool,  $\text{Na}_2\text{SO}_4$  alone, or with a small amt. of dextrin should be used, never NaCl.

L. W. RIGGS

**Regenerating spent bowking liquors (NaOH).** M. FRISBERGER. *Textilber.* 2, 345-8(1921).—Spent liquors may be regenerated by boiling them in the kier after adding  $\text{Ca}(\text{OH})_2$  and enough bleaching powder to impart a yellow color without leaving an excess, and then adding a sulfite or bisulfite. Fats, wood gum, and colored substances are the chief impurities, and these form insol. compds. which are drawn off as sludge. W. F. FARAGHER

**The reserve action of manganese oxides under vat blue.** R. HALLER. *Textilber.* 2, 173-4(1921).—Although a ground of Mn bister ( $\text{Mn}_2\text{O}_3$  and not, as formerly assumed  $\text{MnO}_2$ ) gives dyeings of deepened shade, Mn salts act as a reserve when used according to Ger. patent 215,128. According to this patent, the fabric is prep'd. in a soln. of NaOH or of NaOH and  $\text{Na}_2\text{CO}_3$ , each contg. some glue, and is then dried. The reserve of the following compn. is then printed:  $\text{MnCl}_2$  500 g., thickener (1:1) 35 g., kaolin 75 g.,  $\text{Na}_2\text{Cr}_2\text{O}_7$  25 g., and  $\text{H}_2\text{O}$  50 g. In order to det. the reason for the different action of Mn compds. in the 2 cases, expts. with S. and S. dialyzing cells were carried out. It has been proved by H. that  $\text{Mn}(\text{OH})_2$  pptd. from a soln. of  $\text{MnCl}_2$  is oxidized by the addn. of  $\text{Na}_2\text{Cr}_2\text{O}_7$ , and that a brown powder, an adsorption compd. of the approx. formula  $2\text{MnO}_2 \cdot \text{Cr}_2\text{O}_7$ , is obtained. A soln. of  $\text{MnCl}_2$  of the concn. present in the reserve was placed in a dialyzing cell set into a soln. of NaOH (50 g. per l.). After 24 hrs. a flocculent ppt. appears in the NaOH soln., which is shown by the addn. of  $\text{H}_2\text{O}_2$  (brown color) to be  $\text{Mn}(\text{OH})_2$ . The soln. in the cell is neutral and clear. After washing and drying the cell, a layer of  $\text{Mn}(\text{OH})_2$  is found on the outer side of the cell wall, while the inner portions are free from Mn compds. If a hyposulfite vat liquor is dialyzed in the same cell immersed in  $\text{H}_2\text{O}$ , the indigo is found to pass not only through the inner Mn-free portion of the wall, but also through a considerable portion of the zone contg. the Mn compd. The presence of Liesegang rings was shown by the microscope. If the cell contains both  $\text{MnCl}_2$  and  $\text{Na}_2\text{Cr}_2\text{O}_7$ , as required by the reserve paste, and is set into 2% NaOH soln., the behavior is entirely different. Both solns. contain a brown ppt. That in the NaOH soln. is free from Cr, while that in the cell contains Cr. The soln. is found to be colorless, and contains Mn, but no Cr. The inside of the cell is coated with a brown deposit which contains Cr. This is presumably the adsorption compd. mentioned above. Hyposulfite vat liquor placed in the same cell after it has been washed, and dialyzed against  $\text{H}_2\text{O}$ , shows that no indigo penetrates the brown deposit on the inside of the cell. The action of the reserve is, therefore, made apparent by this expt. W. F. FARAGHER

**Fastness of gambines.** H. ROBINSON. *J. Soc. Dyers Colour.* 37, 220-31(1921).—The methods of dyeing and fastness of Fast Green O (paste) (M.), Dark Green (paste) (C.), Resorcine Green, Gambine R, Y and B (B. D.), and Naphthol Green B (C.), on various mordants are given. CHAS. E. MULLIN

**Pigment dyestuffs derived from tannic acid and some aromatic amines.** A. E. EVEREST AND A. J. HALL. *J. Soc. Dyers Colour.* 37, 227-9(1921).—Cotton mordanted with either tannic or gallic acid, or with the acid and tartar emetic, gives brown to yellow-brown shades when treated with diazo compds. The fastest dyeings were obtained from benzidine, tolidine and dianisidine; the naphthylamines were not as fast; and those from benzene derivs. were not fast. Fastness is not much increased by the tartar emetic. Diazotized amines are capable of coupling with oxidized cellulose, but not with cellulose. Brown pigments may be produced by coupling the diazo compd. with either tannic or gallic acid. CHAS. E. MULLIN

**Provisional method on fastness of dyed silk to washing, scouring and fulling.** W. M. SCOTT. *Am. Dyestuff Rep.* 10, 374-5(1922); cf. C. A. 15, 2191.—Specifications are given for washing, scouring and fulling tests. Colors are classified according to

their fastness to treatment with 1% soap soln. at 100, 70, 50 or 30° or with equal vols. of 1% soap soln. and 1% salt soln. at 30°. A list of standards is given consisting of colors which are fast to these 5 tests, resp., and a 6th class which changes shade even in a bath of equal parts of 1% soap and 1% salt.

L. W. RIGGS

**Rapid fast red GL** (Griesheim-Elektron). F. M. ROWE AND E. LEVIN. *J. Soc. Dyers Colourists* 37, 204-5(1921).—A description of the expts. made in proving the above dye to be an alk. paste of naphthol AS and the nitrosamine derived from diazotized *m*-nitro-*p*-toluidine. A table of the properties of diazotized *p*-nitroaniline and aminonitrotoluenes, when coupled with naphthol AS and  $\beta$ -naphthol, is given.

CHAS. E. MULLIN

**Application of sulfur dyes.** V. EMILIO CAGLIOSTRO. *Color Trade J.* 7, 143-7 (1920); cf. *C. A.* 14, 2421, 3323.—The application of S dyes to the various types of cotton materials, paper, linen, etc., and the app. required are discussed. Formulas are given for printing and discharging; a special method of dyeing S blue; and a method of identifying various blacks on cotton. 4 illus. VI. *Ibid* 171-4.—Dyeing thread effects, silk, half silks, wool and leather with S dyes are described. 6 illus.

CHAS. E. MULLIN

**A new ice-red on cotton.** W. KIELBASINSKI AND C. BENEDEK. *Textilber.* 2, 281(1921).—A note dated Sept. 12, 1913. By combining Naphthol AS (anilide of  $\beta$ -hydroxynaphthoic acid, m. 216°) with diazotized *m*-nitro-*o*-anisidine, an exceedingly brilliant bluish red is obtained. The brightness exceeds that from  $\beta$ -naphthol and diazotized *p*-nitro-*o*-anisidine. Combinations of the two give a range of brilliant fast shades. In order to prevent yellowing of the white ground, the Naphthol AS is removed better by soap to which NaOH is added than by soap alone.

W. F. FARAGHER

**Padded dyeings with indanthrene dyes.** W. KIELBASINSKI AND C. BENEDEK. *Textilber.* 2, 281(1921).—A sealed note filed with the International Society of Dye Chemists in 1913. It is not necessary to dry before steaming the fabric which has been padded with the soln. of dye, formaldehyde-hyposulfite and  $K_2CO_3$ .

W. F. F.

**Indanthrene dyes on silk.** H. E. SCHROERS. *Textilber. Wiss. Ind. u. Handel* 2, 38-40(1921).—Indanthrene dyes have been used extensively in America for securing effect threads in fabrics for silk shirts, etc. The following dyes are suitable for silk: Anthroflavone GC, Indanthrene gold-orange G. R. and RRT; Indanthrene orange RT, Indanthrene copper R, Indanthrene brown RR, Indanthrene reddish brown R, Indanthrene scarlet GS powder, Indanthrene red G, Indanthrene pink B, Indanthrene bordeaux B and B extra, Indanthrene violet R extra, RR extra and RT, Indanthrene blue GC and GCD, Indanthrene green B, Indanthrene blue green B, Indanthrene olive G powder, Indanthrene gray B and 3B and Indanthrene brown B double. In order to avoid injury to the luster of the silk by the alkali which is used, glue, glucose, etc., are added to the bath. Many kinds of silk are dyed successfully before boiling-off, the silk being boiled-off subsequently. Weighted silk cannot be dyed with indanthrene dyes or other vat-dyes. Formulas for various shades are included.

W. F. FARAGHER

**Significance of the addition of tin salt in dyeing and brightening alizarin red.** R. HALLER. *Textilber.* 2, 427-8(1921).—A stannic acid sol is formed when small amts. of Sn salt are added to a soln. of soap. If alizarin is added subsequently, the soln. acquires a yellowish red color, which differs from that obtained when alizarin is added to a soln. of soap alone. This color is that of a stannic acid-alizarin adsorption product (lake) which is much yellower than the corresponding Al lake. The more fiery shade of dyeings made with Sn salt is attributable to the adsorption of the stannic acid-alizarin lake by the Ca-Al-alizarin lake on the fibers.

W. F. FARAGHER



**Quantitative relations in fixing alizarin red in cotton-printing.** R. HALLER AND FRIEDRICH KURZWEIL. *Textilber.* 3, 21-3 (1922).—The dyeings were prepd. by a method which gave the following results:—wt. of cotton cloth 16.8678 g.; wt. of oil (Turkey red) after two paddings, 0.7258 g.; wt. of printing paste on piece, 1.4816 g. (all wts. on samples dried at 100°). A sample of the paste was dried and its content of  $\text{Al}_2\text{O}_3$ , CaO, oil, and alizarin detd. The printed cloth was steamed in a Mather-Platt and then steamed for 30 min. at 0.5 atm. Samples were worked 4 times in boiling distd.  $\text{H}_2\text{O}$ , a glass rod being used, and then rinsed in cold distd.  $\text{H}_2\text{O}$ . The %'s and ratios of  $\text{Al}_2\text{O}_3$ , CaO, oil and alizarin in the wash-water and washed cloth were then detd. The %'s of the applied substances found in the wash-water are as follows:  $\text{Al}_2\text{O}_3$  33, CaO 7, alizarin 10, and oil 14. In practice, the removal must be more complete as a result of the more thorough washing with soap. Prints made by using pastes with smaller proportions of  $\text{Al}_2\text{O}_3$ , CaO, and dye were lighter in shade after washing with distd.  $\text{H}_2\text{O}$ , than the standard samples. Some of the alizarin lake which is formed must, therefore, have less intimate contact with the fibers than other portions, and is therefore, easily removed by washing. This same conclusion applies to dyeings with many other dyes, particularly to indigo, the fixation of which is closely akin to that of alizarin red. For producing a given shade, the paste cannot have less than a min. concn. of dye and other substances essential to formation of the lake.

W. F. FARAGHER

**Some applications of the nitrometer.** J. A. WILSON. *Textile Colorist* 44, 300-1 (1922).—The nitrometer is used in the textile lab. for the examn. of hypochlorites,  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{O}_2$ ; and estn. of Cr, Zn, oxalic acid, HCHO, Cl, perborates, etc.

CHAS. E. MULLIN

**Effect of light on fibers dyed with a mixture of chrysianiline and fuchsin.** W. W. PADDON. *J. Phys. Chem.* 26, 288-91 (1922).—Stobbe (cf. C. A. 2, 3026) states that a mixt. of chrysianiline and fuchsin fades faster than either dye by itself. In the tests described by P., 1-g. samples of wool in 250 cc. of bath were used. Samples were dyed in baths contg. 30, 75, and 150 mg. of chrysianiline, resp., also in baths contg. 30, 75, and 150 mg. of fuchsin, resp. These served as standards for each dye by itself. Samples were dyed in sep. baths contg. 4 different concns. of chrysianiline, then in sep. baths contg. 4 different concns. of fuchsin, also in 4 baths with fuchsin first, then with chrysianiline and finally samples were dyed in baths contg. the mixed dyes in 4 different proportions. When samples that were first dyed with fuchsin were placed in the chrysianiline baths they bled to a marked degree, showing that to some extent chrysianiline replaces fuchsin. The dyed fibers were exposed to the violet carbon arc of a "Fade-ometer," 3 hrs. exposure to this light being equiv. to 5 hrs. exposure to Arizona sunlight. Results showed that chrysianiline alone on the fiber was much more fugitive than any of the mixts. of the 2 dyes tried. Mixed colors fading first were those in which the min. amt. of fuchsin used was present. Samples dyed with fuchsin alone or with mixts. contg. an excess of fuchsin over chrysianiline, the fuchsin being applied last, had not faded in 205 hrs. These expts. and the results of a study of the action of light on water solns. of the dyes prove that fuchsin is remarkably fast and protects chrysianiline from the action of light.

L. W. RIGGS

**Printing fabrics with ultramarine.** G. STRIN. *Textilber.* 2, 176-7 (1921).—Ultramarine in the form of the finest powder is most suitable, since it adheres best to the fibers. Addn. of starch, dextrin, etc. decreases the affinity of the fibers for the particles of ultramarine. If the particles are large, and are held on the fibers by starch or gums, fastness to rubbing and washing are poor.

W. F. FARAGHER

**Testing fabrics.** HERMANN ALT. *Textilber.* 2, 301-3, 311-3, 326-9, 397-8, 414-5, 430-2 (1921).—Fabrics used by the artillery companies (sail-cloth, drill, etc.) have been

tested for resistance to rotting action of soil, impermeability to water, tensile strength when wet, effect of freezing when wet, effects of acids, etc. Complete tables and graphs are given.

W. F. FARAGHER

**Status of German fiber substitutes.** EMIL NEUMANN. *Textile World* 61, 2955-6 (1922).—A general article upon *Vistra*, a cotton substitute; *Lanofil*, a wool substitute; *Stapelwaser*, paper yarns, artificial silk, nettle, etc.

CHAS. E. MULLIN

**The scientific foundations of the manufacture of artificial silk.** K. HESS. *Textilber.* 3, 41-6 (1922).—An address.

W. F. FARAGHER

**Measuring stiffness of sized cloth.** A. H. GRIMSHAW. *Textile World* 61, 2965-7 (1922).—A method and simple app. are described for comparing the stiffening value of various sizing and softening materials. A strip of the sized cloth is projected horizontally and the perpendicular deflection is measured.

CHAS. E. MULLIN

**Bleaching of colored cotton goods.** J. M. MATTHEWS. *Color Trade J.* 8, 157-61 (1921).—A small sample of the colored cloth should be run completely through the various boiling and bleaching processes in order to test the fastness of the color to bleaching, as a hypochlorite fastness test may not be sufficient. Boiling should be reduced to a min. and in some cases the use of enzyme products may substitute for the boil. The effect of the alkali boil on some colors may be due to a reducing action brought about by certain products of decompn. formed by the alkali acting upon impurities and size in the cloth. This action of boiling NaOH soln. upon colors may be reduced by the addn. of such substances as Ludigol (the Na salt of *m*-nitrobenzenesulfonic acid), anthraquinonesulfonate, or inorg. oxidants such as K or NaBrO<sub>3</sub>, Mn salts or Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, to the soln. in the kier. A discussion of the fastness of various cotton dyes to these processes is followed by a table showing the fastness of 47 direct dyes to bleaching, boiling 0.2% Na<sub>2</sub>CO<sub>3</sub> soln., and bleeding to white.

CHAS. E. MULLIN

**Cold bleaching and its influence on the durability of laundered cotton-goods.** P. HERRMANN AND H. FREDERKING. *Textilber.* 2, 249-51, 277-8 (1921).—Bleaching in the laundry should be done in a sep. operation subsequent to the washing, and should be effected with cold (room-temp.) solns. and only as inspection shows that bleaching is required. Cold bleaching processes weaken the fibers less than warm or hot bleaching processes. Bleaching in a sep. bath has the advantage of the absence of certain substances, removed in the washing process, which act catalytically to oxidize the fibers or to destroy bleaching agent. Bleached cotton goods was immersed for 15 min. in 15 times its wt. of a clear soln. of Ca hypochlorite (0.5 g. active Cl per l.) at 20°. This treatment was used 50 times, fresh soln. being employed each time. Between treatments, the test pieces were rinsed with cold water, dipped into a dil. soln. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, washed, squeezed by hand, and allowed to dry. After wetting out, to duplicate the conditions in practice, the next treatment with bleach soln. was begun. The pieces lost 9% in breaking strength (warp yarn only was tested), gained 1.2% in elasticity and lost 2.5% of the original wt. The formation of oxycellulose was negligible and was checked at intervals by the methylene blue test. The harmful effect of such a bleaching process is but little greater than that of a washing process of the usual kind employing soap and soda-ash. Combined washing and bleaching processes, in which soap, soda ash, perborates or persulfates are used, which are conducted at higher temps., have been shown by H. to be much more harmful to cotton and linen goods (C. A. 13, 1404).

W. F. FARAGHER

**The influence of the strength of bleaching solution (cold process) on the durability of cotton fabrics.** P. HERRMANN AND H. FREDERKING. *Textilber.* 2, 428-9 (1921); cf. preceding abstr.—The conditions of the former expts. were employed, and

the strength of the soln. of Ca hypochlorite varied. The results when the solns. contained 1.0 and 2.0 active Cl per l. were as follows: Loss of tensile strength, 35.0 and 59.8%; change in elasticity, +5.7 and -20.5%; loss in wt., 7.9 and 8.7%.

W. F. FARAGHER

Influence of temperature on the durability of cotton goods bleached by the cold process. P. HEERMANN AND H. FREDERKING. *Textilber.* 3, 61-3(1922).—Loss of tensile strength is doubled by raising the temp. 7.5° (20° to 27.5°). This is the same effect that Ebert and Nussbaum found for the speed of bleaching and the spontaneous decomn. of the bleaching soln. (Hypochlorite, etc. pp. 227 and 263; cf. C. A. 5, 591).

W. F. F.

The influence of the time of bleaching in the cold process on the durability of cotton fabrics. P. HEERMANN AND H. FREDERKING. *Textilber.* 2, 395-6(1921).—When the time of immersion in a soln. of Ca hypochlorite was increased from 15 min. to 75 min., the tests on cotton and linen, after 50 treatments were as follows: loss in tensile strength, 15.7%; increase in elasticity, 10.2%; and loss in wt., 3.5%.

W. F. FARAGHER

Persulfates as bleaching agents. W. KIND. *Textilber.* 2, 325-6(1921).—Na perborate was found to bleach better and to weaken the fibers of cotton and linen less than K persulfate in most of the tests made. Addns. of Na<sub>2</sub>CO<sub>3</sub> and water-glass gave improved color and lessened the corrosive action on the fibers, the latter having the greater effect. Mixts. of perborates and persulfates offer no special advantages.

W. F. FARAGHER

The inter-relation of mercerization and spinning. HORACE LOWE. *J. Soc. Dyers Colourists* 37, 296-8(1921).—The yarn is mercerized without tension but at the alkali-cellulose stage of max. shrinkage, and while in the plastic state, is stretched back to normal length, and fixed in H<sub>2</sub>O. An increase of 10-40% in breakout strength and 18% in count is claimed for 60/2 yarn.

CHAS. E. MULLIN

Extraction of oils and soap from thrown silk. H. S. MUDGE. *Am. Dyestuff Rep.* 10, 377-80(1922); cf. C. A. 15, 2987.—The following points are considered: (1) effect of solvents upon the unsoaked raw silk, and (2) upon the soaked silk. (3) Whether all of the oil and soap is dissolved, that is, extd. The extg. power of 9 of the common org. solvents was studied on Japan soft gum, Canton hard gum and Japan yellow. MeOH and EtOH gave the highest extn. On Japan soft gum all of the solvents except Et<sub>2</sub>O gave nearly double the ext. for 20 siphonings over that for 10. Silk is amphoteric, possessing an affinity for both slightly acid and slightly basic substances. The amt. of soap or oil contg. the S group of sulfonation which is left on the fiber after soaking is very small. By analysis of the soaking liquids it was found that 80 to 90% of an ordinary fatty oil present in the soaking bath was removed by the silk. Ten % of the soap remains on the silk, and 80% of the S-bearing fat of sulfonated oils remains in the bath as well as any sol. salts from any source. The amt. of silk recovered from the extn. of raw silk with common org. solvents without soaking showed a gain in wt. in 8 of the 9 tests. Acetone or petroleic ether and MeOH 3 to 1, with 7 or 8 siphonings are recommended for the extn. of soap and oil.

L. W. RIGGS

Absorption spectra of triphenylmethane dyes (ADINOLFI) 3.

Trisazo dye. J. DEDICHEN. U. S. 1,416,621, May 16. Metanilic acid, 1-naphthylamine, 1-naphthylamine-6(or 7)-sulfonic acid and 2-amino-6-naphthol-6-sulfonic

acid give a trisazo dye, the Na salt of which is a blackish powder. It dyes cotton reddish blue turning to bluish gray on diazotization and combination with 2-naphthol or *m*-tolylenediamine.

**Diazo dye.** W. M. RALPH and L. H. FLETT. U. S. 1,415,704, May 9. A union dye, dyeing silk, cotton and wool or mixts. greenish black shades is prepd. by diazotizing *p*-nitroaniline, coupling with 1,8-aminonaphthol-4-sulfonic acid (S acid) and reducing the nitro groups. The dyeings on the fiber may be developed with  $\beta$ -naphthol, *m*-phenylenediamine, *m*-tolylenediamine and similar substances to give greenish or reddish black shades.

**Dyeing and printing textiles.** C. ARIS. Brit. 176,343, Feb. 17, 1922. In dyeing or printing with aniline black the aniline or like body is used in admixt. up to 2% with an "azo-, quinone-, or nitroso-deriv. of aniline, toluidine, or xylydine or of its derivs. by oxidation, reduction, methylation, or by introduction of groups of another order"; the following substances are specifically mentioned: azobenzene, azobenzoic acid, azophenylene, hydrazobenzene, "phenyl-quinone diamine" or isomers thereof, diazoaminobenzene, aminoazobenzene, azoxybenzene, quinone oximes. The specification further describes the use of  $\text{FeCl}_3$  as O carrier in the production of aniline black by known processes or by the process described above, but using a smaller proportion of acid than heretofore; the  $\text{FeCl}_3$  is advantageously employed together with  $\text{NH}_4\text{Cl}$ ; an example of the method is given.

**Dyeing cellulose acetate.** R. CLAVEL. Brit. 176,535, Dec. 14, 1920. Cellulose acetate is dyed with acid, basic, or direct dyes, in baths contg. at least one chloride and an acid, with or without protective colloids. Suitable chlorides are  $\text{NH}_4$ , K, Na, Ba, Mg, stannous, or Zn; formic and acetic are suitable acids; the protective colloid may be gelatin, albumin, boiled-off liquors, tannates, soaps, sulfonated fatty acids, etc. The dyeing is preferably effected in a foam bath as described in 102,310 (C. A. 11, 709) and 103,638 (C. A. 11, 1754).

**Dyeing skins or hairs.** O. KALTWASSER and H. OEHRN. U. S. 1,416,646, May 16. The material is treated with an oxidizing agent such as  $\text{H}_2\text{O}_2$  in the presence of 5-nitro-2-amino-1-hydroxybenzene and  $\text{NH}_3$  soln. A yellow or brown color results.

**Apparatus for dyeing and winding thread or yarn.** E. A. THOMPSON. U. S. 1,415,964, May 18.

**Dyeing-apparatus, etc.** B. F. TOUCHSTONE, T. E. GARDNER, J. A. BANGLE, D. M. SULLIVAN and J. E. HARDIN. Brit. 176,429, Oct. 29, 1920. Warps, etc., in sheet form are passed from section beams or direct from bobbins or spools around submerged rollers in a boiling or conditioning box, a washing-box, dyeing-vats, a hot-water washing-box and a cold-water washing-box and next around intergearing steam-heated drying-cans and then through a compensating-frame and a slashing-machine directly to the loom beam, the dye-vats being uniformly and continuously replenished with dye stock to maintain const. the strength of the dye therein. Various sections of the warps may be dyed different colors, by passing them through different dye-vats, while another section may be undyed, the various sections being maintained sep. from one another until they have dried by using rollers provided with spaced circumferential guiding-flanges, while in some cases the first drying-can is similarly flanged. The washing-vats, etc., may be omitted. When dyeing with indigo, the warps are passed around rollers on an oxidizing-frame. The warps are drawn through the various vats by squeezing-rollers, the lower rollers of which are driven by bevel-gearing from a shaft, which may be driven by an elec. motor arranged midway thereof. The slashing-

machine is driven by belt-gearing from the shaft of one of the drying-cylinders, this shaft being driven by a belt from one of the rollers whereby the warps may be fed through the various parts of the app. at a const. speed. A suitable app. is specified.

**Washing-blue.** J. J. REICHERT. Brit. 176,747, June 13, 1921. A liquid washing-blue having bleaching and disinfecting properties is prepd. by intimately mixing a filtered warm soln. of ultramarine with a soln. of borax in  $H_2O_2$  soln., turpentine, alc., water-glass,  $Na_2WO_4$  and HCHO, heating in an autoclave to about  $50^\circ$ , and stirring vigorously again. In an example, 40 kg. ultramarine are heated to  $38^\circ$  mixed with 8 kg. water at  $38^\circ$ , and the mixt. is heated to  $65^\circ$  or more for some time before being filtered through asbestos. There are then added in succession, with about 10 min. stirring after each addn., 10 kg. borax in 2.18 kg. of 1%  $H_2O_2$ , 10 kg. turpentine, 18 kg. alc., 9 kg. waterglass of  $38-40^\circ$  B $\acute{e}$ , 2 kg.  $Na_2WO_4$  and 2 kg. HCHO.

**Treating knitted fabrics.** M. J. J. NICOLAS. Brit. 176,361, Feb. 23, 1922. To prevent the unmeshing of knitted fabrics, especially silk stockings, the part which begins to become unmeshed is treated with a liquid or pasty substance adapted to become hard on exposure to air and preferably non-colored. Suitable substances are japan or resin varnish, and collodion varnish.

**Preserving cellulose viscose compositions.** W. O. MITSCHERLING. U. S. 1,415,040, May 9. About 1% of  $Na_2S_2O_5$  is used as a preservative in the manuf. of threads, filaments, etc.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

**Barytes and mineral colors.** J. C. BROWN. *Bull. Indian Ind. Labor* No. 22, 45 pp. (1922).—A summary of the industrial uses of barytes and natural earth pigments, specifications and standards of quality demanded by the trade, general methods of marketing, sources of competing supply, description of the minerals, their distinctive characteristics, and their occurrence in India.

F. A. WERTZ

**Whitewashes and aqueous lime paints.** G. J. FINK. *J. Ind. Eng. Chem.* 14, 503-11 (1922).—Exposure tests on 175 formulas for whitewashes shows that those contg. siccatives are very much more permanent, and that casein and linseed oil are the best binders. Water-sol. binders such as glues, are not so good for exterior use.  $Na_2PO_4$  proved to be the best salt for accelerating the soln. of the casein, and the addition of hardening agents such as HCHO to render the film less sol. considerably improved their durability. NaCl and alum added to whitewashes contg. no definite siccativ improved their workability and permanence. Several formulas tested were found superior to most of those in common use. Compn., results of inspection, etc., are tabulated. Illus.

F. A. WERTZ

**Drying of tung oil.** MASAO NONAKA. *J. Chem. Ind. (Japan)* 24, 1272-96 (1921).—The tung oil used was from *Aleurites fordii*. The oil was about 1 year old, and had d<sub>44.4</sub> 0.944, sapon. no. 188, I no. 164.2, acid no. 2.84, Reichert-Meissl value 1.4 and contained 0.75% unsapon. substance. The mixed fatty acids were composed of 82.5% eleomargaric acid, 15.0% oleic acid and 2.5% stearic acid. Conditions that influence the drying of this oil were investigated. The speed of drying is inversely proportional to thickness of the oil. In daylight it dries in 5 days; and contrary to general belief, it dries even in dark (50 days). In absence of air or in a  $CO_2$  atm. it dries. High humidity retards drying, and its wt. increases. The higher the temp. the more quickly

it dries. Driers accelerate the drying in proportion to their quantity. Manganese drier is more effective in dry air than lead drier, but in moist air lead drier is more effective. When the oil is heated, it becomes a viscid transparent, yellow solid. In absence of air it solidifies in 6.3 hrs. at 200°, instantaneously at 250°, but in the air, it requires 11 hrs. at 150° and 3.5 hrs. at 200°. It does not increase in wt. until it dries, then its increase is rapid.  $\text{CO}_2$  and unsatd. compds. are found in the decompd. product of the drying. One of the double bonds of eleostearic acid is easily oxidized. Drying of the oil is due not to oxidation, but to polymerization and condensation. In consequence of polymerization and condensation of unsatd. acids, mols. are aggregated and colloidal soln. is produced. Oxidation accelerates drying indirectly by forming condensation products of the oxidized product. The results of microscopic examn. of dried films are reported.

S. T.

Linseed oil substitutes. W. FAHRION. *Chem. Umschau*, 29, 103-5, 111-3, 120-2 (1922).—A report by Committee D of the Scientific Div. of the Commission for Vegetable and Animal Oils and Fats. The extreme need of linseed oil in Germany during the war led to numerous govt. decrees regulating its use. A fairly good substitute was found in coumarone resin, obtained as a by-product from solvent naphtha purification. Its production was increased to 10000 tons per yr. and was supervised by the govt. Poppy oil would have been an excellent substitute but was needed for food. Paints made from whale, seal, or cod-oil produced sticky films. No substitute made from native materials has been found.

P. ESCHER

Qualitative tests for lead, manganese and cobalt in boiled oils and varnishes. H. VOLLMANN. *Farben-Ztg.* 27, 1943-5(1922).—Pb, Mn and Co can of course be detd. by the usual qual. tests on the ash of the varnish. A more rapid test for Pb is to shake the varnish dild. with benzine, with dil.  $\text{K}_2\text{Cr}_2\text{O}_7$  soln. when  $\text{PbCrO}_4$  forms between the aq. and oily layers. If the dild. varnish is shaken with  $\text{H}_2\text{O}$  contg. a little KOH, a few drops of the aq. layer added to a soln. of benzidine in AcOH gives an intense blue color if Mn or Co is present. A very good test for Mn is to dissolve the ash in HCl, add concd.  $\text{K}_2\text{C}_2\text{O}_4$  and then  $\text{NaNO}_2$  soln., which on addition of  $\text{H}_2\text{O}_2$  produces an intense red. Co is present if a red color is produced in the aq. layer when the dild. varnish is shaken with a soln. of  $\alpha$ -nitroso- $\beta$ -naphthol. Another sensitive test for Co is the blue color produced with  $\text{NH}_4\text{SCN}$ . This test can be applied to a soln. of the ash in HCl or to the aq. ext. obtained by shaking the varnish dild. with benzine, with dil. HCl. Shaking of the varnish with  $\text{NH}_4\text{SCN}$  soln. does not give the test directly because even small amts. of rosin interfere with the reaction so that the procedure must be modified: To 1.5 cc. of the dild. varnish add 0.5 cc. concd.  $\text{NH}_4\text{SCN}$  soln., 0.25 cc. amyl alc., and 3 or 4 cc.  $\text{Et}_2\text{O}$ , and shake. In most cases the  $\text{Et}_2\text{O}$ -alc. layer will be red owing to traces of Fe. On this account add 1 cc.  $\text{AcONH}_4$  soln. and 2 to 3 drops tartaric acid, when the varnish- $\text{Et}_2\text{O}$ -alc. layer is mostly greenish in the presence of Co, but shaking with 1 cc.  $\text{Me}_2\text{CO}$  will bring out the characteristic blue color. The usual methods of test are reviewed.

F. A. WERTZ

Reports on lac, turpentine, and rosin. ANON. *Indian Trade Inquiry, Imp. Inst.* 74 pp.(1922); *J. Soc. Chem. Ind.* 41, 203R(1922).—The report of a special committee makes recommendations for improving the efficiency of the industry, maintaining standards of purity and quality, and increasing production of Indian gums, resins, turpentine, and essential oils; and gives present production statistics. Cf. *C. A.* 15, 3909.

F. A. WERTZ

The late Mr. Holman Hunt's experiments on the permanency of artists' oil colors. A. P. LAURIE. *J. Royal Soc. Arts* 70, 432-8(1922).—In 1870 Holman Hunt exposed a large number of artists' colors on canvas. Inspection of these colors shows that the

present selected lists of artists' pigments are reliable with the possible exception of pale Cd yellow and Co yellow; that the present practice of protecting by an easily removable mastic varnish is justified; and that excessive darkening of the oil on this canvas is probably due to Pb driers, which are excluded from the oils and varnishes used in modern practice. Discussion. F. A. WERTZ

The graphic inks. HANS WAGNER. *Chem.-Ztg.* 46, 421-4(1922).—A review of the compn., manuf., and uses of printing inks for newspaper and book printing, steel and copper plate printing, three color processes, etc. F. A. WERTZ

Some experiments on the separation of resin acids in the liquid resin from the sulfate (pulp) process (EVLER) 23. Chief constituents of Japanese lac (MAJIMA) 10.

ANTHONY, W.: Die Anstrichfarben und ihre Bindenmittel in Farbenhandel. Ein Ratgeber für Farben-Händler und Verbraucher. 2nd Ed. Berlin S. W. 19: union Deutsche Verlagsgesellschaft, 24 M.—Reviewed in *Farben-Ztg.* 27, 2087-8(1922).

White pigment. H. R. RAFSKY. U. S. 1,415,391, May 9. A fine grained pigment is obtained by reaction in  $H_2O$  between slaked magnesian lime and  $Na_2CO_3$ .

Paint resistant to fire and water. A. H. MIKESSELL. U. S. 1,415,380, May 9. A paint adapted for use on wood, Fe, brick or concrete is formed from casein in borax soln. 25 lbs., "magnesite residue" 72.5 lbs. and  $H_2O$  60 gals.

Printing processes. E. AURICH and F. WOLF. *Brit.* 176,599, Jan. 26, 1921. Designs in the form of a light color on a dark ground are printed lithographically from a stone or grained metal surface on which the design is drawn in a rapid-drying grease-resisting ink. The design is drawn in reverse, and the whole of the stone and design is coated with a greasy printing-ink which resists and repels water. The whole is then treated with a soln. of  $H_3PO_4$  in gum, gummed, and washed with turpentine which removes the greasy ink from the design, and thins it on the background, and finally by rubbing with water the ink is removed from all parts of the design. The final print gives a light design on a dark ground. The design is preferably drawn in an ink formed of 1 oz. of  $H_2O$ ,  $\frac{1}{2}$  oz. of  $H_3PO_4$  in 16 oz. of gum,  $\frac{1}{4}$  oz. of lamp-black water-color,  $\frac{1}{4}$  oz. of lamp-black,  $\frac{1}{4}$  oz. of oxalic acid, and 3 drops of glycerol, and the greasy printing-ink is preferably formed of 1 oz. of asphalt dild. in turpentine, 1 oz. of turpentine,  $\frac{1}{2}$  oz. of black printing-ink, and  $\frac{1}{8}$  oz. of ether.

Polishing composition for use on painted or enameled surfaces. J. M. INOUE. U. S. 1,415,570, May 9. An emulsified mixt. of HOAc (5.5%) 49.2, turpentine 8.9, boiled linseed oil 15.8, benzyl ester 1 and solids from oxidized cider 1.5 parts.

Coumarone resin. L. RABINOVITZ. U. S. 1,416,062, May 16. The coumarone in solvent naphtha is polymerized by the action of concd.  $H_2SO_4$  (66° B $\acute{e}$ .) while agitated and the resin is afterward hardened by heating to about 180° in a high vacuum. The product has an I no. below 50.

## 27—FATS, FATTY OILS AND SOAPS

R. SCHERUBEL

Baskerville method of refining vegetable oils. P. T. WHESTER. *Cotton Oil Press* 5, No. 5, 36-8.—The Baskerville process for refining vegetable oils (*C. A.* 15, 320, 606) under factory conditions gives a better break and more easily filtered ~~oils~~

than are obtained by the best preliminary test with 500-cc. samples in the lab. Data from lab. refinings of 38 samples of soy-bean, peanut, cottonseed and coconut oils show in all cases the best refining by the Baskerville process gives a lower loss than by the old method. Because a soap stock which is firm and porous rather than coherent is desired it is best to work with strong NaOH solns. 25° Bé. usually gives satisfactory results.

H. S. BAILY

Composition of soy-bean oil. W. B. SMITH. *J. Ind. Eng. Chem.* 14, 530-1 (1922).—The compn. of soy-bean oil having an I no. of 134 is approx. as follows: 2 to 3% linolenic, 55 to 57% linolic, 26 to 27% oleic, and 9 to 10% satd. acids. E. SCHERUBEL

Culture and experimentation with the oil palm. M. TEISSONNIER. *Bull. mat. grasses inst. colonial Marseille* 1921, 198-200.—Phys. and chem. analysis of soils suitable for growing oil palms are given.

E. SCHERUBEL

Soap Stock Committee of A. O. C. S. Supplemental report. C. P. LONG. *Cotton* 5, No. 5, 38-9 (1922).—Convention discussion of Soap Stock Committee Report (C. A. 15, 3405) and a method for prepg. "well mixed" sample of soap stock as follows. Transfer the entire sample to a mixing pan and weigh both, place the pan on a steam bath and stir into the soap stock, soda ash to take up excess of H<sub>2</sub>O. Bring the total wt. of the pan and soap stock back to the original wt. by adding more soda ash or heating longer to evap. more H<sub>2</sub>O. Thus prepd. the sample is homogeneous and representative portions may be readily withdrawn for analysis.

H. S. B.

Transparent glycerol soft soaps. G. Seifensieder *Zig.* 49, 259-62, 279-81 (1922).—G. describes the manuf. of K soaps. The customary addition of 12-20% (basis of 80% KOH) mixt. of K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> must be carefully proportioned to obtain the desired permanent consistency in cold and hot weather, but no general rule can be given to suit all cases. As a filler is used 11-14° Bé. K<sub>2</sub>CO<sub>3</sub> or 9-12° Bé. KCl soln. up to 20% on the fat basis. Directions are given for testing and regulating at the kettle the proper amt. of filler, and for the proper care of the finished soap while in storage. P. E.

Grained potash soaps from natural fats. LEGRADI. *Seifensieder Zig.* 49, 237-8 (1922).—L. was able to salt out K soaps of tallow-fatty acids by the use of KOAc soln., which latter could be used over a second time. The resulting solid K soap had the appearance of a dark Na soap. A trial to salt out a K soap prepd. from a "S-oil" also yielded a solid soap but it was necessary to salt it out 3 times.

P. ESCHER

The clarification of liquid soap. E. C. ALFORD. *Am. Perfumer* 17, 143 (1922).—The usual method is to mix 1 to 2% of infusorial earth with the finished soap, agitate the batch and pump it through a filter press provided with a specially woven filter cloth. The best method of installation is to have a pump with a capacity larger than that of the filter press, and by-pass part of the liquid back to the tank. The liquid thus returned agitates the batch sufficiently to prevent settling of the infusorial earth. For 2000 gallons per 10-hr. day, the filtration cost exclusive of overhead would be approx. \$0.004 per gal. The use of a filter press as indicated renders possible the use of a poorer grade of oil or fat, inasmuch as any dirt present is removed from the finished soap. A sketch is given showing a general layout of a plant for filtering soap. W. O. E.

Effect of high concentration of salt on the viscosity of a soap solution. ANNIE M. KING. *J. Soc. Chem. Ind.* 41, 147-8T (1922).—A pure prepn. of Na palmitate was made up to a concn. of 1/2 mol. wt. to 1 kg. of boiled H<sub>2</sub>O. To a portion of this stock soln. ignited NaCl was added to make the 0.5 N palmitate also 0.88 N NaCl. This is the max. concn. of NaCl which can be added without formation of 2 layers. The falling-ball method was used to det. the viscosity of this soln. and then more of the stock soln. was added so as to dil. the NaCl while normality of the palmitate was kept const. A



series of solns. of decreasing NaCl content was measured; thereupon successive portions of NaCl were added so as to check the previous results by passing through the same range of concns. in the opposite direction. The results were calcd. from the formula  $\eta = K(s-D)T$ , where  $K$  = the tube const.  $\eta_1/(s-\sigma)T_1$ ,  $\eta$  = viscosity of soap soln. at 80.85° in c. g. s. units,  $s$  the d. of steel ball = 7.806,  $D$  the d. of soap soln.  $T$  the time of fall in soap soln.,  $\eta_1$  the viscosity of castor oil of d. = 0.96 at 24.1° = 7111 c. g. s. units, and  $T_1$  is the time of fall in castor oil = 4 sec. There is a max. viscosity in the soln. which is 0.5  $N$  with respect to both the palmitate and chloride; and this figure lies between 10.1 and 10.6. McBain and collaborators have shown that in moderately concd. solns. the Na palmitate in the absence of NaCl is a colloidal electrolyte partly dissociated into Na ions and the corresponding ionic micelle. Addition of NaCl drives back the dissociation so that the soap is present as neutral colloid which is heavily hydrated and which is the chief factor in causing the high viscosity. Further addition of NaCl diminishes the hydration of the neutral colloid in the same way that still higher concns. have been shown to diminish that of curd fibers of the palmitate. Solns. of K oleate with increasing aunts. of KCl were observed and it was noted that while the addition of NaCl causes the clear liquid to set to a transparent jelly without impairing the homogeneity of the soln., a much greater amt. of NaCl is required to cause formation of 2 liquid layers and finally formation of curd. E. SCHERUBEL.

**Spontaneous heating of soap powder (sapo medicatus).** M. WEGNER. *Chem. Umschau* 29, 119-20, 127-9(1922).—A medicinal powdered soap, prepd. according to the German Pharmacopeia, but from olive oil alone instead of a 1:1 mixt. of lard and olive oil, was packed in 10-kg. paper bags in a wooden box which stood free by itself. It became heated in one of the paper bags sufficiently to cause smoking. Analyses indicated normal conditions and absence of peroxides of fatty acids in the unchanged soap and formation of lactones in the heated portion of the soap. Heating expts. with the original soap powder, before and after extg. it with gasoline to remove the 1.17% free fat which it contained, showed that both samples increased in temp. spontaneously at 151-190° and at 123-192°, resp. No specific cause could be found to explain the heating of the soap while in storage. P. ESCHER.

**Spontaneous heating of soaps.** A. WELTER. *Chem. Umschau* 29, 151-2(1922).—W. describes the spontaneous heating of 500-600 kg. of cold, dry, powdered cottonseed-oil soap on a concrete floor; it burned to a coke-like mass within 15 min. P. E.

**The cleansing effect of soap solutions.** R. T. A. MEES. *Z. deut. Öl-Fett-Ind.* 42, 235-7, 250-2; *Chem. Weekblad* 19, 82-5(1922).—M. discusses the cleansing effect of soaps, more especially the work of M. Fishier who shows that the cleansing power runs parallel to the amt. of liquid soap gel present, and McBain who introduces the idea of the colloidal ion of fatty acids, thereby explaining the two contradictory properties in soap solns. *vis.*, of conducting the elec. current and of being retained by a dialyzing membrane. M. also discusses the work of Langmuir, who establishes the mol. orientation of fatty acids: the hydrocarbon chain of the acid standing vertical on the  $H_2O$  surface, its carboxyl group on top. Harkins' work demonstrates that the introduction of Na oleate in the benzene- $H_2O$  interface reduces the surface tension to zero, because the mol. orientations becomes: benzene mol. against the hydrocarbon chain of Na oleate and the  $H_2O$  mol. against the reactive pole of Na oleate; no work is therefore required to increase the surface and no force is present to decrease it, resulting in a permanent emulsion. The gel theory requires little soly. of the cleansing medium in the adjoining phases; the orientation theory demands a polar character in the cleansing medium; the greater the polar difference the less sol. is the substance. This polar diff. increases with the length of the C-chain, reaching a max. in Na palmitate. But the polar diff.

does not diminish soly. in the interface, since here only the poles dissolve in the related solvents and since both poles are occupied, the product is more stable than the hydrated soap gel itself, so that the latter will push off its mols. toward the oil-H<sub>2</sub>O interface and increase their concn. there, a condition which is essential for a permanent emulsion. The impurities in dirty wash belong to 3 classes: (1) Water-sol. or polar substances, (2) insol. or inactive substances, mainly hydrocarbon oils, (3) earthy, inactive substances. These active and inactive characteristics find their counter-part in the soap mol. and this is the essential point of the cleansing effect of soaps. Some earthy substances like kaolin also concentrate at the oil-H<sub>2</sub>O interface and are capable of being wetted by oil and H<sub>2</sub>O; for these reasons such substances likewise have cleansing power.

P. ESCHER

Chlorine determination in silica-containing washing compounds. G. BRUHNS. *Seifensieder Ztg.* 49, 262(1922).—Cl detns. by Mohr's method with AgNO<sub>3</sub> soln. can be made in the presence of dissolved or gelatinized SiO<sub>2</sub> by first neutralizing with HNO<sub>3</sub> against phenolphthalein and then by finely dividing the SiO<sub>2</sub> by shaking or rubbing and addition of considerable H<sub>2</sub>O. The drying of SiO<sub>2</sub> to make it insol. becomes unnecessary.

P. ESCHER

The effect of electrolytes on the constitution of soap solutions (SALMON) 2. The constitution of soap solutions (MCBAIN, *et al.*) 2. Some experiments on the separation of fatty acids in the liquid resin from the sulfate (pulp) process (BULGER) 23. Catalytic decomposition of oleic acid (MAILHE) 10. Purifying oils and solvents (Brit. pat. 176,540) 13.

MARCUSSON: Die Untersuchung der Fette und Öle. Halle a. S.: W. Knapp. M 31.80, bound 37.20.

Sulfoaromatic compositions for decomposing fats. A. GODAL. U. S. 1,416,284, May 16. A mixt. of oleic or other fatty acid and aromatic substance such as C<sub>10</sub>H<sub>8</sub> is sulfonated at a temp. below the m. p. of the mixt. in the presence of a solvent such as C<sub>6</sub>H<sub>6</sub>.

Catalyst. K. H. WIMMER. U. S. 1,416,249, May 16. A formate of a catalytic metal such as Ni is treated with a protective substance such as oil and then reduced by heating with H or water gas to obtain a catalyst adapted for use in hydrogenating oils.

Apparatus for extracting oils, fats or greases from nut kernels, oil meal or similar materials. H. ENGL. U. S. 1,415,433, May 9.

Cleansing compositions. F. G. CHADBOURNE. Brit. 176,577, Jan. 10, 1921. Addition to 160,892 (C. A. 15, 2559). In the prepn. of a compn. of soap and china clay as described in the principal patent, the clay mixed with the fatty acids is the finest obtained centrifugally, *e. g.*, in the centrifugal separator described in 113,326. The particles of the clay used have an av. diam. of 0.00004 in.

Soap powder. A. IMHAUSEN. Brit. 173,791, July 6, 1920. Soap powder is produced by cooling the hot liquid mixt. of soap and soda or other filler, preferably while in motion, to below the temp. of the atm., even to below 0°, and gradually reheating to the air temp. by a heating medium. The cooling may be effected by blowing in cold air, or by the admixt. of liquid air or other gas which bleaches the powder as it is reheated, or by satg. the hot liquid in a closed vessel with air or other gas, leaving the mass under gaseous pressure to loosen and disintegrate, and blowing it in finely divided

condition into a well cooled chamber; or the cooling and reheating may be effected by jacketing the contg. vessels or by flowing the mass in thin films on to internally cooled or heated rollers. The mixt., when cooled to  $0^{\circ}$ , may be allowed to absorb liquid hydrocarbon or other solvent of fat, preferably made water-sol., to produce a durable soap powder contg. volatile solvents. A suitable app. is specified.

Shaving soaps, cosmetics, etc. M. H. JOLIVET. Brit. 173,767, Jan. 3, 1922. Shaving-soap sticks, make-up crayons, or other sticks or blocks are protected by a coating of stearin, paraffin or other wax, or other substance that is preferably inert and strongly adhesive to the block and without appreciable action on the skin or other surface on which the block is used.

Emulsifying resin soap. O. KAMM. U. S. 1,415,363, May 9. Resin size contg. free resin is incorporated in sufficient  $H_2O$  to yield a substantially clear emulsion when the mixt. is heated to near the b. p., thus forming an emulsion which is stable at the b. p. and which may be indefinitely dild.

Forming soap into cakes. E. M. LOVELAND. U. S. 1,416,483, May 16. Mech. features.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Sugar in the year 1921. H. C. PRINSEN-GHEERLIGS. *Australian Sugar J.* 13, 712-14(1922).—A review of the economic situation in Cuba and Java and of beet sugar in Europe. I. D. GARARD

The sugar and distillation industries in Brazil. DESMET. *Bull. assoc. chim. suc. dist.* 39, 264-8(1922).—An address on the state of these industries. I. D. G.

Report of the committee on manufacturing progress in Louisiana. *Louisiana Planter* 68, 174-175(1922).—A record of economies which have been effected and which should be made in manufacturing is given. C. H. CHRISTMAN

Sugar refining in Louisiana with Norit. W. H. DUNSTONE, JR. *Louisiana Planter* 68, 254-6(1922).—This work was done in a raw-sugar house which had been equipped for producing granulated sugar. Regular practice is followed in producing the first massecuite. The washings from this are used to mix with the sugar obtained from the second massecuite and this is added to a first massecuite in a mingler prior to purging. A raw sugar of 99 purity is thus obtained. It is melted down with clear water to  $56^{\circ}$  Brix, strained, heated and sent to the Norit tanks. After agitation with Norit it is pumped to the plate and frame presses. Five tanks of liquor 4000 gallons each contg. 700, 400, 300, 200, 200 lbs. Norit, resp., are pumped in the order given into two presses and after the liquor is expelled the cakes of Norit are cut down and divided among 3 tanks of liquor; 900 lb. is used in one tank and 450 lb. each in the other 2 tanks. The third use of this Norit is made by placing 900 lb. in each of 2 tanks. After this use it is dropped into a tank of water and heated prior to pressing for sweetening off. The sweet water showed a purity of 97-98. The sweetened Norit is sent to the kilns and burned at  $1100^{\circ}$  F. A bag filter is used as a precaution against breaks or leaks in the press cloths. The boiling of the liquor is made in 4 stages, but all the strikes are mixed before drying. Periodical boiling of Norit with 2% HCl and with 5% NaOH is relied upon to remove excess ash. 93 lb. of standard granulated sugar from 100 lb. of 96 test is obtained regularly. C. H. CHRISTMAN

Making invert sugar from sucrose. T. S. HARDING. *Sugar* 24, 140-2(1922).—The nature, prepn. and uses of invert sugar are specified. Particular attention is given

to the properties of invertase solns., and their use in making invert sugar. Expts. are reported showing the effect of the amt. of invertase, temp. and other variables upon the completeness of the inversion of sucrose. For large-scale work a ton of sugar dissolved in 1200 gallons of water should be inverted in 5 days if 5 gallons invertase soln. is used. Cf. C. A. 16, 353.

C. H. CHRISTMAN

A precipitate obtained from cane juice after clarification with kieselguhr and decolorizing carbon. VICTOR BIRCKNER. *Louisiana Planter* 68, 285-6(1922).—Sirups treated with kieselguhr and decolorizing carbon, instead of  $\text{SO}_2$  and lime, developed a grayish gelatinous ppt. when evapd. in the effects. The analysis of the ppt. showed it contained 79.4% ash. The analysis of the ash gave the compn.,  $\text{SiO}_2$ -25.6,  $\text{P}_2\text{O}_5$ -21.7,  $\text{SO}_3$ -3.2,  $\text{CaO}$ -10.0,  $\text{Fe}_2\text{O}_3$ -4.1,  $\text{ZnO}$ -6.7,  $\text{MnO}$ -0.6%, with carbonates present. The analytical methods used are given. The source of this ppt. is attributed in part to the clarifying agents used but, in the main, to the ash content of the raw cane juice.

C. H. CHRISTMAN

**Boiling house recoveries.** RAYMOND ELLIOTT AND J. C. CHAPMAN. *Hawaiian Planters' Records* 26, No. 2; *Facts about sugar* 14, 310(1922).—A system of ash sucrose control was run over a 6-week period, with the idea of comparing the recoveries so obtained with the calcd. S. J. M recoveries and with the actual recoveries. The formula used for calcg. the recovery from sirup was that of Peck: Recovery = (Ash sucrose ratio of molasses—Ash sucrose ratio of juice)/(Ash sucrose ratio of molasses—Ash sucrose ratio of sugar). The same formula was also used, substituting the ash sucrose ratio of the massecuite in question for that of the juice. This gave very good results with first massecuite, but with second and third massecuites the difficulty in obtaining samples made it unfeasible. The results indicate that the theoretical yield as calcd. by the ash sucrose formula checked very well with that calcd. by the S. J. M. formula, especially when based upon the sirup. The use of mixed juice in this connection entails two extra ash detns. and a rather involved calcn. There could be no advantage in using the mixed juice in a mill where the remelt is not returned to process before the evaporators. Sirup would be the logical material to use in such a case.

N. KOPFLOFF

**Juice heater calculations.** P. H. PARR. *Intern. Sugar J.* 23, 675-7(1921).—This is an elaboration of the ordinary formula for logarithmic temp. difference into a form applicable to the case of two heaters in series, each with a different steam temp., where only the initial and final temp. of the fluid being heated is known.  $S_1$  = steam temp. in first heater,  $S_2$  = steam temp. in second heater,  $J_1$  = liquid temp. entering first heater,  $J_2$  = liquid temp. leaving first heater and entering second,  $J_3$  = liquid temp. leaving second heater,  $\Delta_1 = S_1 - J_1$ ,  $\Delta_2 = S_1 - J_2$ ,  $\Delta_3 = S_2 - J_2$ ,  $\Delta_4 = S_2 - J_3$ ,  $\theta$  = coeff. of heat transmission,  $W$  = heat transferred per hr. per unit of surface per heater  $\theta = \theta/W$  and is a measure of the rate of heating. The usual logarithmic formula for mean temp. then can be transformed to give

$$\left\{ \begin{array}{l} \Delta_2 = \Delta_1/e^{\theta} \\ \Delta_4 = \Delta_3/e^{\theta} \end{array} \right\} \dots\dots\dots (1)$$

$$a = \log_e (\Delta_1/\Delta_2) = \log_e (\Delta_3/\Delta_4) \dots\dots\dots (2)$$

$$\Delta_4 = \Delta_1/e^{2a} + \frac{(S_2 - S_1)}{e^a} \dots\dots\dots (3)$$

$$a = \log_e \frac{S_2 - S_1 + \sqrt{(S_2 - S_1)^2 + 4 \Delta_1 \Delta_4}}{2 \Delta_1} \dots\dots\dots (4)$$

Several problems are worked out, in which the applicability of these formulas is demonstrated.

W. L. BADGER

Tables for the determination of sucrose by double polarization before and after diastatic inversion. H. COLIN. *Bull. assoc. chim. suc. dist.* 39, 258-62(1922).—The advantages of diastatic inversion are: (1) The sucrase acts in neutral or slightly acid medium which is the same for both polarizations. (2) The enzymic activity is considerable at room temp.; it increases to about 55°. (3) The action of the ferment is scarcely affected by the presence of neutral salts which retard the action of acids (*C. A.* 13, 2142). (4) A small portion of the diastatic liquor is sufficient, hence the impurities do not affect the polarization. The wt. in g. of sucrose is given by  $\pi = (\alpha_1 - \alpha_2)/A$  in which  $\alpha_1$  is the initial rotation,  $\alpha_2$  the rotation after the inversion and  $A$  is  $\alpha_1 - \alpha_2$  for a 1% soln. of sucrose. One table gives values for  $A$  for a 50-cm. and a 20-cm. tube at all temps. from 0° to 30° and another gives  $\pi$  between 10° and 25° for values of  $\alpha_1 - \alpha_2$  from 0.6° to 4.0°. The results will be in error if there are other sugars present which are affected by the enzyme, especially raffinose.

I. D. GARARD

A new type of saccharimeter. ROBERT GALLOIS. *Bull. assoc. chim. suc. dist.* 39, 212-15(1921).—The instrument, which is mounted on an axis adjustable in height and in the direction it may be pointed, will take tubes of any model up to 50 cm. The compensator is entirely inclosed, the scale is transparent and well lighted, and it contains a key by which the scale may be adjusted.

I. D. GARARD

The twenty-gram normal weight polariscope in the raw sugar factory. J. C. QUEVEDA. *Louisiana Planter* 68, 316-8(1922).—A table is given which furnishes in detail the coeff. of purity for juices, molasses, massecuites when the saccharimeter readings are based on a 20-g. normal wt. Suggestions are made concerning the advantage of the 20-g. normal wt. in the detn. of glucose ratio.

C. H. CHRISTMAN

Burning of sugar cane fields. ANON. *Sugar* 24, 246-8(1922).—Special plots of cane were burned and harvested together with control plots immediately and after 5, 10 and 15 days. A marked deterioration set in on the burned cane at once and immediate harvesting was proved desirable. A loss of 3 1/8% per day in sugar is estd.

C. H. CHRISTMAN

Commercial development of the Genter process for continuous treatment of carbonatation juices. A. L. GENTER. *Sugar* 24, 223-6(1922).—The principles incorporated in this continuous thickener make it possible to handle the juices economically. The char filtrate coming through the thickener comprizes 80% of the total feed. The mud which contains 20-22% solids is then sent to vacuum rotary filters and freed from sugar liquors. The final mud contains 0.1-0.2% sucrose. The purity and concn. of lime salts remains unchanged in the thickening process. One man can handle the station for 1500 tons of beets daily, and with one man at the vacuum filters, the recovery of sugar is made more efficient.

C. H. CHRISTMAN

Economy in milling. L. W. HOFLAND. *Louisiana Planter* 68, 176-8(1922).—Greater care in regulating the feed of the mills results in better extn. A thick blanket with slow movement through the mills gives best results. Reabsorption of juice is favored more in mills equipped for gripping the bagasse rather than for pressing.

C. H. CHRISTMAN

The calorific value of bagasse. P. H. PARR. *Intern. Sugar J.* 24, 13-8(1922).

W. L. OWEN

Starch and glucose from maize. I. JOSEPH BURTT-DAVY. *S. African J. Ind.* 5, 130-6(1922).—A review of the manuf. and uses of corn oil, gluten and their by-products.

WM. STERICKER

Dakamballi starch. J. A. GOODSON. *Analyst* 47, 205-6(1922).—Analysis of Dakamballi starch from the fruit of *Aldina insignis* gave in %: H<sub>2</sub>O 19.57, fat 0.04, protein (N  $\times$  6.25) 1.25, crude fiber 0.10, EtOH-sol. and cold H<sub>2</sub>O-sol. traces, ash:

(21, starch (by the method of Davis and Daish, *C. A.* 8, 2636) 76.1, alkaloids and cyanogenetic glucosides none. It was of a pale brown color and was tasteless. The starch granules were 11–42 $\mu$ , mostly circular, with a few truncated and ovate. The hilum was at the broader end, with well marked concentric rings. In mucilage form it is used in British Guiana for dysentery.

C. C. DAVIS

Compounds of iodine with the components of starch. H. v. EULER AND KARL MYRBAECK. *Ann.* 428, 1–24(1922); cf. *C. A.* 15, 2364.—A starch soln. which has been heated only a short time will take up considerably more I than one heated a longer time. After 0.5 hr. the change is very slight. The relation between the concn. of the I and the amt. absorbed is studied; it appears that the amt. of I absorbed depends upon the partial pressure of the soln. Apparently the absorption proceeds in 2 steps. The appearance of the blue color bears no relation to the concn. of the starch. C. J. W.

The importance of carbohydrates in present-day economy. P. HAAS. *Pharm. J.* 108, 222–4; *Chemist and Druggist* 96, 347–8(1922).—An address, dwelling on the formation of carbohydrates in plants, and the technical uses of sugars, starches and cellulose.

S. WALDBOTT

Constitution of starch and glycogen (KARRER) 10.

SCARD, FREDERIC I.: Cane Sugar Factory. New York: Book Dept. of "Sugar," 153 Waverly Pl. \$1.25. Reviewed in *Sugar* 24, 338(1922).

"Saccharine trap" for sugar solution evaporators. G. ENGEL, SR. U. S. 1,415,818, May 9.

## 29—LEATHER AND GLUE

ALLEN ROGERS

The reactions involved in the preparation of leather. E. STIASNY. *Naturwissenschaften* 10, 175–9(1922).—A review.

C. C. DAVIS

Analysis of 123 cases of anthrax in the Pennsylvania leather industry. H. F. SMYTH AND ELIZABETH BRICKER. *J. Ind. Hyg.* 4, 53–62(1922).

E. J. C.

Histological examination of skin. M. L. KRALL. *Cuir* 11, 185–7(1922).—Pieces of pelt, 1–2 cm. long and 0.5 cm. wide, are fixed (I) by treatment in successive baths of (a) HCHO, acetic and picric acid mixt., (b) 3 baths of EtOH of increasing strength (c) CHCl<sub>3</sub>-toluene mixt., (d) toluene (e) toluene-cedar oil mixt., (f) 3 baths of melted paraffin for 24 hrs. at 58–59°, or (II) by freezing with EtCl or liquid CO<sub>2</sub>, preceded by treatment with K<sub>4</sub>Cr<sub>2</sub>O<sub>7</sub>-Na<sub>2</sub>SO<sub>4</sub> soln. or 5% HCHO. Sections may then be cut with a microtome as usual. Tanned leather requires no fixation prior to sectioning.

F. L. SEYMOUR-JONES

The factors influencing the plumping of hides in tan liquors. W. R. ATKIN. *J. Soc. Leather Trades' Chem.* 6, 138–44(1922).—A discussion of the swelling of hides in tan liquors on the basis of the Procter-Wilson-Loeb theory. The presence of tannin decreases the swelling of hide powder by acid. For detg. the swelling power of tan liquors the use of the lime-water titration, H-ion concn. detn., and the measurement of the direct swelling of hide powder is recommended.

F. L. SEYMOUR-JONES

The dyeing and tanning of leather. VI. JOHN HELFRICH. *Color Trade J.* 7, 83–5(1920); cf. *C. A.* 13, 2615; 14, 3337.—A discussion of the use of natural dyewoods and exts., acid and chrome dyes; methods of dyeing and app.; and finishing methods and app.

CHAS. E. MULLIN

**Formaldehyde tannage.** A. M. HGV. *J. Soc. Leather Trades' Chem.* 6, 131-6 (1922).—Pieces of ox-hide were tanned with HCHO in buffer solns. and the  $p_H$  of solns. and pelt detd. colorimetrically before and after tannage. Tannage is incomplete where the  $p_H$  of the pelt is below its iso-electric point ( $p_H$  4.8). Excess concn. of OH ions ( $p_H < 9.5$ ) yields a hard and swollen leather, tanned only on the exterior. For complete tannage the pelt must be kept on the alk. side of its iso-electric point.

F. L. SEYMOUR-JONES

**The manufacture of animal materials into gelatin and glue.** RICHARD KISSLING. *Chem.-Ztg.* 46, 113-6, 151-3(1922).—A review, with numerous German patent references, of the manuf. of *gelatin* and *glue* from hide and leather scrap, hides, bones, fish scrap, and cadavers of animals.

WM. STERICKER

**Artificial leather.** R. B. RESPASS. U. S. 1,416,064, May 16. A felted fabric is satd. with a binder such as a rubber or cellulose compn. and the sheet thus prepd. is pressed and dried and coated with a leather dressing.

**Tanning hides and skins.** E. W. MERRY. U. S. 1,415,671, May 9. Leather resistant to heat and moisture is prepd. by treating hides with a pyrophosphate and alum and then with a Cr tanning compn.

**Depilating hides, etc.** T. B. CARMICHAEL and W. H. OCKLESTON. Brit. 173,788, July 2, 1920. Relates to processes for unhairing hides and skins by means of  $Na_2S$  and NaOH and consists in the use of these substances in successive and very weak solns. of a strength of approx. 0.5%. Dry hides are preferably first softened in a 0.3%  $Na_2S$  soln., being then treated in a 0.5% soln. followed by treatment in a 0.5% soln. of NaOH. In an example 3 pits or drums are employed contg., resp., 30, 56, and 52 lb. of material to 1,000 gal. of  $H_2O$ , the liquors being replenished for each batch of hides and fresh liquor prepd. at intervals, the depleted second sulfide bath being used for the preliminary soaking when the first bath is renewed for use as the second bath.

